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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

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RESEARCH PAPER RP1612

Part of Journal of Research of the National Bureau of Standards, Volume 33, November 1944

THERMAL-DENSITY COEFFICIENTS AND HYDROMETER CORRECTION TABLES FOR VEGETABLE TANNING EXTRACTS

By Mary Grace Blair and Elmer L. Peffer

ABSTRACT

Densities and thermal expansions have been determined of the vegetable tanning extracts—quebracho, oak bark, hemlock bark, chestnut, and mangrove bark—within the range 1.00 to 1.12 specific gravity at 60°/60°F and over the temperature range 50° to 100° F. Thermal-density coefficients are presented in such a manner that the density of an extract at any temperature within the range can be calculated if its specific gravity at 60°/60° F or its density at 25° C is known. The information obtained has been used also in the preparation of tables for correcting hydrometer readings at observed temperatures in degrees Barkometer, in degrees Twaddle, and in degrees Baumé to readings at the standard temperature 60° F.

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I. INTRODUCTION

In the leather-tanning industry the specific gravity of a tanning extract is used in conjunction with other data accumulated for that particular extract to measure the strength of the tannins present. Three types of hydrometers with scales based on specific gravity—Barkometer, Twaddle (also spelled Twaddell), and Baumé—are in common industrial use. Each of these hydrometers is standard at 60° F. In general, it is impracticable to cool each sample to this temperature before observations are made. The much quicker method of reading the hydrometer at any temperature and applying a correction to obtain the true value at the standard temperature is preferred.

In view of the extensive use of hydrometers at tanneries, The American Leather Chemists Association suggested that the National Bureau of Standards check the barkometer correction table in most common use, extend this table, and prepare tables for Twaddle and Baumé hydrometers. The Association supplied samples of extracts considered to be representative of the chief tanning extracts. The samples

included hemlock bark, oak bark, quebracho, chestnut, and mangrove bark ("cutch") extracts. Thermal-density coefficients of these extracts were determined and are presented in such a manner that they may be used to change true specific gravity at 60°/60° F to density or specific gravity at other temperatures. Their application in the calculation of hydrometer corrections is also discussed. A table for use in correcting the readings of hydrometers graduated in specific gravity units is presented. The values for barkometer, Twaddle, and Baumé scales calculated from these results will be found in tabular form in National Bureau of Standards Circular C449, Hydrometer Correction Tables and Thermal Density Coefficients for Vegetable Tanning Extracts.

II. PROCEDURE

As the tanning extracts are used in various strengths, density determinations were made of diluted samples covering the range of the barkometer hydrometer, 0 to 120 degrees barkometer or 1.00 to 1.12 specific gravity at 60°/60° F. Water in sufficient amounts, calculated with the original density of the extracts as the basis, was added to known weights of the extracts to produce samples with specific gravities of approximately 1.03, 1.06, 1.09, and 1.12. One sample, mangrove bark extract, which was supplied in solid form, was dissolved and diluted to the required specific gravity by the aid of the hydrometer.

Diluting the samples caused precipitation of colloidal matter in most cases, the amount of precipitation increasing with the extent of the dilution. The picnometers were filled while these finely divided solids were still homogeneously mixed with the solution. Their settling to the bottom in subsequent determinations did not produce any apparent irregularities in the data.

Densities were determined at 10°, 20°, 25°, 30°, and 40° C by the picnometer method, that is, by weighing a picnometer of known volume filled in a constant temperature bath adjusted to the desired temperature. Calculation of density was made with correction for the buoyancy of air.[1]

III. REDUCTION OF OBSERVATIONS

The rate of change of density with change of temperature was calculated from the observed densities by the application of the method of least squares.

It is assumed that the expansion of any sample may be represented by an equation having the form

$$D_t = D_T + \alpha_T(t-T) + \beta_T(t-T)^2 + \gamma_T(t-T)^3, \quad (1)$$

in which

D_t = density at any temperature, t
D_T = density at the standard temperature, T
α_T, β_T, γ_T = constant coefficients determined for each sample.

[1] More detailed description of the method and the picnometers used may be found in Tech. Pap. BS 7, 8 (1916) and in Bul. BS 8, 371 (1913) S197.

If the observation equations derived by substitution of the observed values in equation 1 are added, an expression is found for D_T as a function of the mean density $[D_i]_m$. Calculation of the constants of the density equation has been simplified by the symmetrical selection of the temperatures of observation. Thus, the relationship of D_T to $[D_i]_m$ becomes

$$D_T=[D_i]_m-[C_1^2]_m\beta_T.$$

The observation equations may now be written in the form

$$C_1\alpha_T+C_2\beta_T+C_3\gamma_T=N.$$

α_T, β_T, and γ_T are calculated from the normal equations

$$\begin{aligned}\sum C_1^2\alpha_T+\sum C_1C_2\beta_T+\sum C_1C_3\gamma_T&=\sum C_1N\\ \sum C_1C_2\alpha_T+\sum C_2^2\beta_T+\sum C_2C_3\gamma_T&=\sum C_2N\\ \sum C_1C_3\alpha_T+\sum C_2C_3\beta_T+\sum C_3^2\gamma_T&=\sum C_3N,\end{aligned}$$

in which

$$\begin{aligned}C_1&=t-t_m \qquad (t_m=\text{mean temperature})\\ C_2&=C_1^2-[C_1^2]_m \qquad ([C_1^2]_m=\text{mean } C_1^2)\\ C_3&=C_1^3\\ N&=D_t-[D_i]_m \qquad ([D_i]_m=\text{mean } D_i).\end{aligned}$$

The various steps in obtaining the constants for expressing density at any temperature in terms of density at 25° C are illustrated by the sample calculation, which shows the operation for liquid quebracho extract diluted to approximately 1.06 g/ml. Table 1 shows computation of the coefficients to be substituted in the normal equations. The normal equations become

$$\begin{aligned}500\alpha_{25}+102500\gamma_{25}&=-0.16945\\ 52500\beta_{25}&=-0.20325\\ 102500\alpha_{25}+22812500\gamma_{25}&=-34.69225\\ D_{25}&=1.06813-100\beta_{25}.\end{aligned}$$

By solving these equations, the following values of

α_{25}, β_{25}, γ_{25}, and D_{25} are obtained:

$$\begin{aligned}\alpha_{25}&=-0.0003440\\ \beta_{25}&=-0.00000387\\ \gamma_{25}&=+0.000000025\\ D_{25}&=1.06852.\end{aligned}$$

These values when substituted in the equation

$$D_t=D_{25}+\alpha_{25}(t-25)+\beta_{25}(t-25)^2+\gamma_{25}(t-25)^3, \qquad (2)$$

which is derived from the general equation 1, give the density values shown in table 2.

TABLE 1.—*Sample of reduction of observations*

t	C_1	C_1^2	C_3	C_1C_3	C_1C_2	C_3^2	C_2C_3	C_3^3	D	N	C_1N	C_2N	C_3N
10	−15	225	−3375	−1875	+50625	15625	−421875	+11390625	1.07272	+0.00459	−0.00988	+0.57400	−15.40800
20	−5	25	−125	+375	+625	625	+9375	+15625	1.07013	+.00200	−.01002	−.15030	−.25050
25	0	0	0	0	0	10000	0	0	1.06852	+.00039	−.00000	−.03920	−.00000
30	+5	25	+125	−375	+625	625	−9375	+15625	1.06670	−.00143	+.00715	+.10725	−.17875
40	+15	225	+3375	+1875	+50625	15625	+421875	+11390625	1.06257	−.00366	+.06540	+.69500	−18.76500
		5)500		0	102500	52500	0	22812500	5)5.34094		−0.16945	−0.20325	−34.69225
		100							1.06813				

TABLE 2.—*Calculation of D_t*

t	$t-25$	$(t-25)^2$	$(t-25)^3$	$\alpha(t-25)$	$\beta(t-25)^2$	$\gamma(t-25)^3$	D_t, calculated	D_t, observed	Difference (cal.—obs.)
10	−15	225	−3375	+0.00516	−0.00087	−0.00000	1.07272	1.07272	0.00000
20	−5	25	−125	+.00172	−.00010	.00000	1.07014	1.07013	.00001
25	0	0	0	.00000	.00000	.00000	1.06852	1.06852	.00000
30	+5	25	+125	−.00172	−.00010	.00000	1.06670	1.06670	.00000
40	+15	225	+3375	−.00516	−.00087	+.00008	1.06257	1.06257	.00000

TABLE 3.—*Thermal-density coefficients for tanning extracts*

Tanning Extract	D_{25}	$\alpha_{25}\times10^{6}$	$\beta_{25}\times10^{7}$	$\gamma_{25}\times10^{9}$
Quebracho (from International Products Corporation)	1.19642	−487	−28	+2
Do	1.12156	−405	−34	+2
Do	1.09205	−371	−35	+1
Do	1.06111	−336	−41	+4
Do	1.03080	−298	−43	+2
Quebracho (SM brand)	1.22126	−515	−23	+1
Do	1.12170	−407	−34	+2
Do	1.09110	−370	−36	+1
Do	1.06852	−344	−39	+2
Do	1.03101	−300	−43	+3
Oak bark (from Teas Extract Co.)	1.23230	−507	−33	+6
Do	1.10959	−378	−37	+2
Do	1.08402	−349	−40	+3
Do	1.06100	−321	−42	+2
Do	1.03143	−292	−47	+3
Hemlock bark (from Teas Extract Co.)	1.18890	−466	−28	+2
Do	1.11899	−389	−36	+5
Do	1.08573	−356	−40	+5
Do	1.06155	−323	−42	+2
Do	1.03067	−291	−48	+4
Chestnut (from Mead Corporation)	1.11351	−384	−37	+1
Do	1.08500	−351	−40	+2
Do	1.07203	−334	−43	+1
Do	1.03004	−296	−45	+3
Solid Mangrove bark, "cutch"	1.11851	−385	−33	0
Do	1.08104	−349	−39	+4
Do	1.04903	−308	−43	+1
Do	1.02422	−288	−45	+3

The thermal-density coefficients for each sample calculated according to the above method are listed in table 3 and are shown graphically in figure 1. It will be noted that the α values for the various extracts are close together. The best straight line fitting all the data was determined by the method of least squares. This line is shown in figure 1. Equations of the β and γ lines of figure 1 were calculated likewise. The lines have the following equations:

$$\alpha_{25}=0.0008586-0.0011184\ D_{25}, \tag{3}$$
$$\beta_{25}=-0.00001421+0.00000950\ D_{25},$$
$$\gamma_{25}=+0.0000000297-0.0000000044\ D_{25}\ (=+0.000000025 \text{ over the density range of this project}).^{2}$$

Calculated from equations 3	*Calculated from Chappuis' data*
$\alpha_{25}=-257\times10^{-6}$	$\alpha_{25}=-257\times10^{-6}$
$\beta_{25}=-47\times10^{-7}$	$\beta_{25}=-48\times10^{-7}$
$\gamma_{25}=+3\times10^{-8}$	$\gamma_{25}=+3\times10^{-8}$

The equations provide a ready means for obtaining the coefficients α_{25}, β_{25}, and γ_{25} for tanning extracts of any given density within the range of observations. Thus, if the density of a tanning extract is known at 25° C, its density at any other temperature may be computed.

[2] The coefficients for water were not included in the derivation of this set of equations. However, Chappuis' data on water recalculated in the same manner, Bul. BS **9**, 401 (1913) S197, agree well with those calculated for D_{25}=0.99708. The values are not strictly comparable, since Chappuis' values are for air-free water.

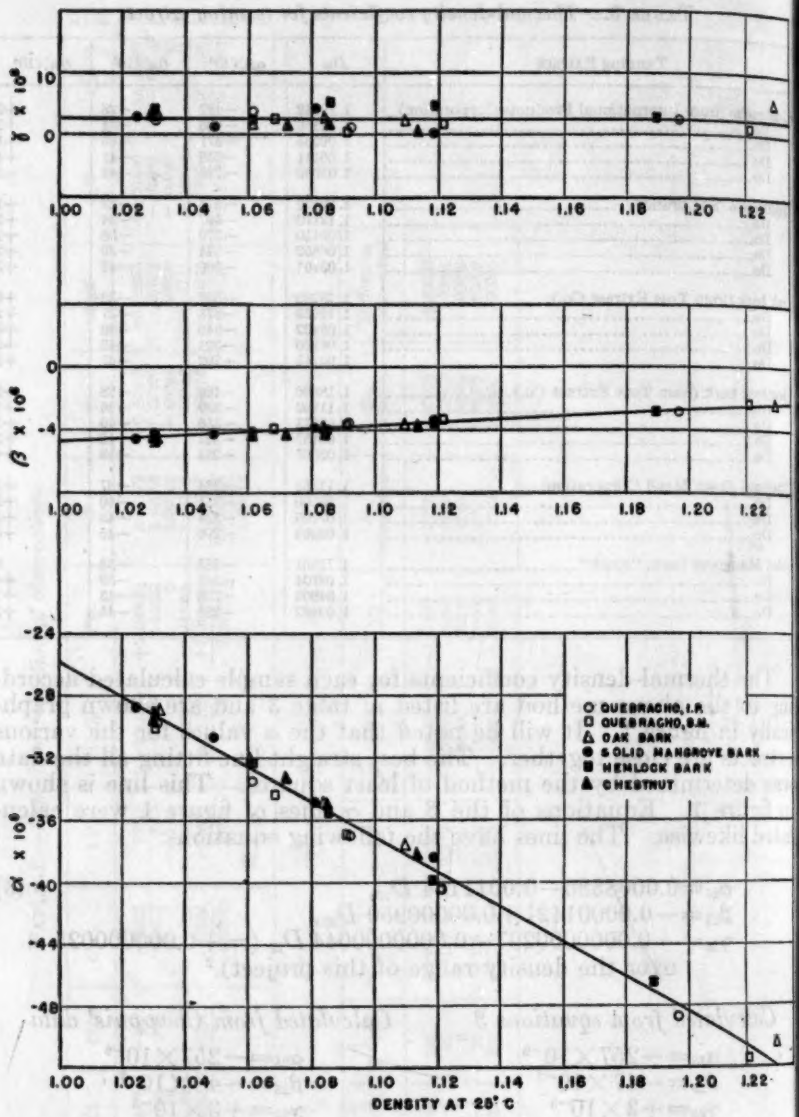

FIGURE 1.—*Thermal-density coefficients α, β, and γ as functions of density.*

IV. TRANSFORMATION OF DATA TO 60° F

The coefficients given in the preceding section apply only at 25° C. However, barkometer, Twaddle, and Baumé hydrometers (the hydrometers usually employed for measuring the densities of tanning extracts) are all standardized at 60° F. Consequently, equation 2, representing the expansion of the tanning extracts at 25° C, and the corresponding coefficients have been transformed in such a way that by their use the density at any temperature can be calculated from the density at 60° F (15.56° C). When so transformed the equation becomes

$$D_t = D_{15.56} + \alpha_{15.56}(t-15.56) + \beta_{15.56}(t-15.56)^2 + \gamma_{15.56}(t-15.56)^3, \quad (4)$$

in which

$$\alpha_{15.56} = \alpha_{25} + 2\beta_{25}(15.56-25) + 3\gamma_{25}(15.56-25)^2$$
$$\beta_{15.56} = \beta_{25} + 3\gamma_{25}(15.56-25)$$
$$\gamma_{15.56} = \gamma_{25}.$$

The density at 15.56° may be obtained from density at 25° C by use of equation 2.

Use of the transformed equation 4 is still dependent indirectly through the coefficients upon density at 25° C. However, a table of relationships may be set up easily over the desired range between density at 25° C; density at 15.56° C (computed from density at 25° C); and $\alpha_{15.56}$, $\beta_{15.56}$, and $\gamma_{15.56}$ (computed from α_{25}, β_{25}, and γ_{25}).

For calculation of the hydrometer correction tables the equation has been transformed still farther. Changed to a specific gravity basis, the equation becomes

$$\text{Sp gr}\,\frac{t}{15.56} = \text{Sp gr}\,\frac{15.56}{15.56} + \alpha_{\frac{15.56}{15.56}}(t-15.56) + \beta_{\frac{15.56}{15.56}}(t-15.56)^2 + \gamma_{\frac{15.56}{15.56}}(t-15.56)^3. \quad (5)$$

The coefficients $\alpha_{\frac{15.56}{15.56}}$, $\beta_{\frac{15.56}{15.56}}$, and $\gamma_{\frac{15.56}{15.56}}$ of this equation are equal to the corresponding coefficients $\alpha_{15.56}$, $\beta_{15.56}$, and $\gamma_{15.56}$ divided by the density of water at 15.56° C. Table 4 provides numerical values for these coefficients. Hence, by the combined use of table 4 and equation 5, the specific gravity of a vegetable tanning extract at any temperature within the range may be calculated from its specific gravity at 60°/60° F.

TABLE 4.—*Thermal density coefficients for tanning extracts for use with equation (5)*

Specific gravity at $\frac{15.56°}{15.56°}$ C $\left(\frac{60°}{60°}\text{ F}\right)$	$\frac{\alpha_{15.56}\times 10^3}{15.56}$	$\frac{\beta_{15.56}\times 10^7}{15.56}$	$\frac{\gamma_{15.56}\times 10^8}{15.56}$
1.000	−160	−54	+3
1.005	−167	−54	+3
1.010	−173	−54	+3
1.015	−180	−53	+3
1.020	−186	−53	+3
1.025	−192	−52	+3
1.030	−199	−52	+3
1.035	−205	−51	+3
1.040	−212	−51	+3
1.045	−218	−50	+3
1.050	−224	−50	+3
1.055	−231	−49	+3
1.060	−237	−49	+3
1.065	−244	−48	+3
1.070	−250	−48	+3
1.075	−256	−48	+3
1.080	−263	−47	+3
1.085	−269	−47	+3
1.090	−275	−46	+3
1.095	−282	−46	+3
1.100	−288	−45	+3
1.105	−294	−45	+3
1.110	−301	−44	+3
1.115	−308	−44	+3
1.120	−314	−43	+3

V. CALCULATION OF HYDROMETER CORRECTIONS

By use of equation 5, specific gravities at 10°, 20°, 25°, 30°, 35°, and 40° C with reference temperature 15.56° C were calculated corresponding to each specific gravity at 15.56°/15.56° C at intervals of 0.005 throughout the desired range. These calculated specific gravities represent the readings on hydrometers which are correct, respectively, at the temperatures of the calculation. The corresponding readings on hydrometers standardized at 60°/60° F were found by applying the conversion of density basis formula for hydrometers. [3]

$$\text{Sp gr}\,\frac{t}{15.56°\text{C}} = \text{Sp gr}\,\frac{15.56°\text{C}}{15.56°\text{C}} + \Delta\,\text{Sp gr}\,\frac{15.56°\text{C}}{15.56°\text{C}},$$

in which $\Delta = 0.000023\ (15.56 - t)$.

Interpolation was used to find the hydrometer readings at the temperature intervals corresponding to the same true specific gravity at 60°/60°F. These values were plotted, one axis representing temperature and the other representing the hydrometer reading. A series of smooth curves was obtained consisting of a curve for each true specific gravity. From each curve were read the hydrometer readings for each degree change in temperature. The table was completed by interpolation to obtain columns for each 0.001 change in specific gravity. The table is given in abbreviated form with this paper. See table 5.

[3] The hydrometers are assumed to be made of glass with a coefficient of cubical expansion equal to 0.000023 per degree centigrade. This figure in the equation may be replaced by the proper coefficients and tables calculated for hydrometers of other kinds of glass, or the tables presented here may be used with hydrometers of other glasses if a correction is applied to the reading of the hydrometer to obtain the corresponding reading on a hydrometer of glass with a coefficient equal to 0.000023 per degree centigrade. The correction is $+(\alpha - 0.000023)\ (15.56 - t)\ R$, in which R is the reading of the hydrometer made at temperatures t, and α is the coefficient of the glass of which the hydrometer is made.

The largest error that is made by the use of the present table for Pyrex hydrometers without applying a correction is only 0.00036 in specific gravity (0.4° bk). This error would occur at the maximal density and temperature.

TABLE 5.—*Hydrometer correction data*

Reduction of observed specific gravities to specific gravities at 60°/60° F.

Observed temperature	Observed specific gravity						
	1.0000	1.0200	1.0400	1.0600	1.0800	1.1000	1.1200
	Corresponding specific gravity at 60°/60° F						
°F							
----------	----------	1.0193	1.0391	1.0590	1.0788	1.0987	1.1186
----------	----------	1.0193	1.0392	1.0591	1.0790	1.0988	1.1187
----------	----------	1.0194	1.0393	1.0592	1.0791	1.0989	1.1188
----------	----------	1.0194	1.0394	1.0593	1.0792	1.0991	1.1190
----------	----------	1.0195	1.0395	1.0594	1.0793	1.0992	1.1191
----------	----------	1.0196	1.0395	1.0595	1.0794	1.0993	1.1192
----------	----------	1.0197	1.0396	1.0596	1.0796	1.0995	1.1194
----------	----------	1.0197	1.0397	1.0597	1.0797	1.0996	1.1196
----------	----------	1.0198	1.0398	1.0598	1.0798	1.0997	1.1197
----------	----------	1.0199	1.0399	1.0599	1.0799	1.0998	1.1198
----------	1.0000	1.0200	1.0400	1.0600	1.0800	1.1000	1.1200
----------	1.0001	1.0201	1.0401	1.0601	1.0801	1.1001	1.1202
----------	1.0001	1.0202	1.0402	1.0602	1.0803	1.1003	1.1204
----------	1.0002	1.0203	1.0403	1.0604	1.0804	1.1004	1.1205
----------	1.0003	1.0204	1.0404	1.0605	1.0806	1.1005	1.1207
----------	1.0004	1.0205	1.0406	1.0606	1.0807	1.1008	1.1208
----------	1.0005	1.0206	1.0407	1.0608	1.0808	1.1009	1.1210
----------	1.0006	1.0207	1.0408	1.0609	1.0810	1.1011	1.1212
----------	1.0007	1.0208	1.0409	1.0610	1.0812	1.1013	1.1214
----------	1.0008	1.0210	1.0411	1.0612	1.0813	1.1014	1.1216
----------	1.0010	1.0211	1.0412	1.0613	1.0815	1.1016	1.1218
----------	1.0011	1.0212	1.0413	1.0615	1.0817	1.1018	1.1220
----------	1.0012	1.0213	1.0415	1.0616	1.0818	1.1020	1.1221
----------	1.0013	1.0215	1.0416	1.0618	1.0820	1.1022	1.1223
----------	1.0014	1.0216	1.0418	1.0620	1.0822	1.1024	1.1225
----------	1.0015	1.0217	1.0419	1.0621	1.0823	1.1026	1.1227
----------	1.0017	1.0219	1.0421	1.0623	1.0825	1.1027	1.1229
----------	1.0018	1.0220	1.0422	1.0625	1.0827	1.1029	1.1231
----------	1.0019	1.0222	1.0424	1.0626	1.0829	1.1031	1.1233
----------	1.0021	1.0223	1.0426	1.0628	1.0830	1.1033	1.1236
----------	1.0022	1.0225	1.0427	1.0630	1.0832	1.1035	1.1238
----------	1.0024	1.0226	1.0429	1.0632	1.0834	1.1037	1.1240
----------	1.0025	1.0228	1.0430	1.0634	1.0836	1.1039	1.1242
----------	1.0027	1.0230	1.0432	1.0636	1.0838	1.1041	1.1244
----------	1.0028	1.0231	1.0434	1.0638	1.0840	1.1043	1.1246
----------	1.0030	1.0233	1.0436	1.0639	1.0842	1.1046	1.1248
----------	1.0031	1.0234	1.0438	1.0641	1.0844	1.1048	1.1251
----------	1.0033	1.0236	1.0439	1.0643	1.0846	1.1050	1.1253
----------	1.0035	1.0238	1.0441	1.0645	1.0848	1.1052	1.1256
----------	1.0036	1.0240	1.0443	1.0647	1.0850	1.1054	1.1258
----------	1.0038	1.0241	1.0445	1.0649	1.0852	1.1057	1.1260
----------	1.0040	1.0243	1.0447	1.0651	1.0855	1.1059	1.1262
----------	1.0041	1.0245	1.0449	1.0653	1.0857	1.1062	1.1265
----------	1.0043	1.0247	1.0451	1.0655	1.0859	1.1064	1.1267
----------	1.0045	1.0249	1.0453	1.0657	1.0861	1.1066	1.1270
----------	1.0047	1.0251	1.0455	1.0659	1.0864	1.1068	1.1272
----------	1.0048	1.0253	1.0457	1.0662	1.0866	1.1070	1.1274
----------	1.0050	1.0255	1.0459	1.0664	1.0868	1.1073	1.1277
----------	1.0052	1.0257	1.0461	1.0666	1.0870	1.1075	1.1280
----------	1.0054	1.0259	1.0464	1.0668	2.0872	1.1078	1.1282
----------	1.0056	1.0261	1.0466	1.0671	1.0875	1.1080	1.1285

Barkometer, Twaddle, and Baumé tables were computed from th specific-gravity table. These tables are not included with this pape but will be published separately in Bureau Circular C449. The scop of the tables is as follows:

Table	Range	Interval
Barkometer	0° to 119° bk	1.0
Baumé	0° to 15° Bé	1.0
Twaddle	0° to 24° Tw	1.0

True values corresponding to the above observed values are given t the nearest 0.1 degree for each degree change in temperature from 50 to 100° F. The relationship between the scales is

$$\text{Sp gr } 60°/60° \text{ F} = \frac{1000 + ° \text{ bk}}{1000}$$

$$\text{Degrees barkometer} = \frac{\text{Sp gr } 60°/60° \text{ F} - 1}{0.001}$$

$$\text{Sp gr } 60°/60° \text{ F} = \frac{1000 + (° \text{ Tw} \times 5)}{1000}$$

$$\text{Degrees Twaddle} = \frac{\text{Sp gr } 60°/60° \text{ F} - 1}{0.005}$$

$$\text{Sp gr } 60°/60° \text{ F} = \frac{145}{145 - ° \text{ Bé}}$$

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Sp gr } 60°/60° \text{ F}}$$

VI. APPLICABILITY AND ACCURACY OF THE COEFFI CIENTS AND DERIVED CORRECTION TABLES

The thermal-density coefficients of equations 3 and table 4 were com puted from the observed densities of several representative tannin extracts. Duplicate observations agree, in general, within three unit in the fifth decimal place of the density value. These observed den sities were subjected to an adjustment by the method of least square to determine the most probable density at each temperature. Hence errors in the original observation and their reduction are small in com parison with the error due to assuming one value for all extracts. Th accuracy of the specific gravity of any particular extract compute from the coefficients is dependent upon the closeness with which th rate of expansion of that particular extract agrees with the composit rate.

Conclusions as to the degree of accuracy obtainable when the com posite coefficients of equations 3 are used may be drawn from an ex amination of the graphs in figure 1. Slight variations between coef ficients of the different types of extracts studied are evident, while th agreement between different brands of the same type is remarkable For example, the points representing the α coefficients of two brand

of quebracho vary little from a straight line, but this line is definitely below the least squares line. Further examination shows the coefficient farthest from the least squares line to be that of quebracho (SM brand) with density 1.12 g/ml. The observed value of α at this point is -407×10^{-6}. The least squares value is -396×10^{-6}. The difference is 0.000011. This difference introduces an error of 0.00016 in the density calculated at 40° C, the temperature farthest from the standard temperature 25° C. When the β and γ values are considered, the difference caused by using the least squares value is 0.00015. Over most of the temperature range and for most of the extracts the discrepancy is much less.

Since the hydrometer correction tables are based on the data discussed in the preceding paragraph, they should be accurate to the same degree if calculated with like sensitivity. Calculation of corrections for the barkometer table was made to 0.1° bk. This hydrometer is usually graduated in degrees barkometer, equivalent to 0.001 sp gr at 60°/60° F. Probable accuracy of the correction table, then, is much greater than that with which the hydrometer is likely to be read.

The barkometer table had been compared with the table [4] supplied by The American Leather Chemists' Association as the basis that is being used in the leather industry. A greater accuracy as well as a greater range has been attempted in the new table. The two agree exactly at low densities and temperatures but diverge as either temperature or density increases. This difference amounts to 1.1° bk for a reading of 60° bk at 100° F, the larger value being given by the new table.

VII. CONCLUSION

The thermal-density coefficients have been presented in such a manner that they may be used for calculation of the density of a tanning extract at any other temperature within the range covered by the investigation if the density at either 25° C or 60° F is known.

Data for correcting hydrometer readings, calculated with the aid of these coefficients, have been prepared in tabular form at the request of the tanning industry to meet the needs of that industry. It is believed that they are applicable to all vegetable tanning extracts included in this investigation without the introduction of errors in excess of those that unavoidably occur in the reading of hydrometers under industrial laboratory conditions.

WASHINGTON, June 27, 1944.

[4] This table may be found in J. A. Wilson, Modern Practice in Leather Manufacture, p. 287 (Reinhold Publishing Corporation, New York, N. Y., 1941).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1613

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MEASUREMENT OF RATE OF FLOW OF WATER THROUGH FILTER PAPER

By Herman Bogaty and Frederick T. Carson

ABSTRACT

A method is described for measuring the rate of filtration of water through filter papers, in which the paper is used as a cone in the usual manner and special apparatus is not required. An equation is derived, with which a water-filtration coefficient is determined from the filtration data. Data are presented also to show the effect of continued filtration on this coefficient. A correlation is shown between the air permeability of filter paper and the rate of filtration, enabling one to make a good estimate of the speed of a filter paper without wetting it. A definite procedure is recommended for determining the rate of flow of water through filter paper.

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I. INTRODUCTION

Suitable filter paper is an item of considerable importance to the analytical chemist. Until recently, most of the filter paper intended for analytical use has come from Germany, England, and Sweden. The war has made the supply from these sources uncertain. As a consequence, American manufacturers have undertaken the making of grades of analytical filter papers that hitherto have not been produced in this country.

Heretofore, the chemist has relied mainly on established brands and grades, with which he has become familiar, as guides in the choice of suitable filter papers. It seems desirable to provide manufacturers and consumers with better means of determining the suitability of filter paper intended for analytical use, especially since new products are now included in the available supply.

An investigation was undertaken at the National Bureau of Standards to supply the needed information. A number of the important physical and chemical properties of available filter papers are being studied, and will in due time be reported upon. One phase of this study is the evaluation of the rate of filtration, or speed, as this prop-

erty is frequently called. This article is confined to reporting the development of a method of measuring the rate of flow of water through filter paper.

II. PREVIOUS WORK

Herzberg[1] used a constant-head apparatus, based on the principle of the Mariotte flask, which forced water through a horizontal disk of filter paper 10 cm^2 in area and discharged it into a measuring flask. With a head of 5 cm of water at 20°C, the instrument was used to measure either the time of filtration of 100 ml of water or the volume of water filtered in 1 minute. He reported a range of filtering rates of 23 to 760 ml/min per 100 cm^2 of area for 30 filter papers.

Griffin and Parish[2] reported difficulty in maintaining a constant head with the Herzberg apparatus, and were unable to obtain consistent results with it. They devised a filtering cell, 2 inches in diameter, in which a horizontal filter circle supported by a wire screen was subjected to a head of 9 inches of water, held constant by overflowing an excess of water at the top of a standpipe. The filtrate was caught in a measuring flask, and the time required to filter 100 ml of water at 20°C was reported. They gave values of 8 to 120 seconds for typical papers. They also gave data on the effect of temperature.

III. CONE METHOD

If one could make suitable measurements of filtration through filter paper folded in the usual manner to form a cone, some obvious advantages would result. Such a procedure would adhere more nearly to the conditions of normal filtering, and there would be no need for special apparatus required when disks are used.

Griffin and Parish observe, however, that, although the most common method of appraising filter papers has been to judge the relative performance when they are folded and supported as cones, several uncertainties characterize such a procedure, making it unreliable and ill-adapted for supplying data suitable for record and reference. They point out that the results depend upon the design of the funnel, its angle, the dimensions of the stem, the manner of folding the filter paper, the amount of water used, and the manner of pouring it in.

These difficulties can be surmounted with little effect on the innate simplicity of the testing procedure. The effect of the funnel can be eliminated by supporting the filter cone freely in a wire loop, or in a conical wire helix if the cone is large. This method of support was used in the tests to be described. The paper can be folded in a standard manner. All the water used was poured in at once.

Of the several factors that ordinarily contribute to the uncertainty in measuring rate of flow through a conical filter, the one which presents the greatest difficulty is the change in head and filtering area as the water level falls in the cone during the testing period. Preliminary experiments with disks of filter paper indicated that Darcy's law should be applicable, that is, for a given filter paper the rate of filtering of water is proportional to the area of the filter and to the head. With this premise a conical filter lends itself readily to the derivation of a water-filtration coefficient.

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[1] W. Herzberg, Papierprüfung [7th ed.] p. 109 (1932). 5th ed. (1921) J. Springer, Berlin.
[2] R. C. Griffin and H. C. Parish, Ind. Eng. Chem. 14, 109 (1922).

Figure 1 represents a 60-degree conical filter made by folding a filter circle in the usual manner. Let k be the water-filtration coefficient, defined as the volume of water filtered per second through unit area under unit head.[3] A quantity of water is poured into the cone, and at any time, t, thereafter, the volume remaining is v, having a depth h.

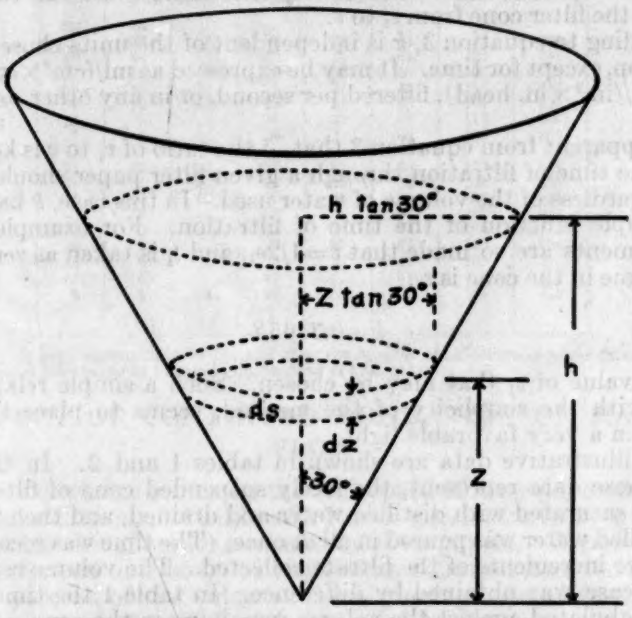

FIGURE 1.—*Sixty-degree conical filter containing water.*

Consider an elementary surface, ds, of the cone at a depth, $h-z$, having a height, dz, a slant height of dz sec 30° ($=2\sqrt{3}/3\ dz$), and a circumference at midheight of $2\pi z$ tan 30° ($=2\sqrt{3}/3\pi z$). Therefore, the area, $ds=4/3\pi z dz$. The rate of flow through any small area is the water-filtration coefficient multiplied by the area and the head operating on that area (Darcy's law). The rate of change of the volume in the cone with time is negative. Hence,

$$dv/dt=-k\int_0^h(h-z)ds=-4/3\pi k(h\int_0^h zdz-\int_0^h z^2dz)=-2/9\pi kh^3. \quad (1)$$

At the time t, the volume of water remaining in the cone is

$$v=1/3\pi h(h\ \tan\ 30°)^2=1/9\pi h^3.$$

Therefore,

$$dv/dt=-2kv. \quad (2)$$

[3] Although the conical filter is composed of three layers over half its area, and only one over the other half, this density distribution is constant for all values of z (fig. 1) and therefore will not affect the setting up or the solution of the differential equations. This fact does mean, however, that k is associated with this particular arrangement of the filter paper and would not have the same value for some other arrangement, such as a disk, for example. The coefficients for disk and cone would, however, be proportional.

The solution of equation 2 gives

$$k=\frac{ln\ v_1/v}{2(t-t_1)}=\frac{1.151\ \log\ v_1/v}{t-t_1}, \tag{3}$$

in which $t-t_1$ is the time interval required to decrease the volume of water in the filter cone from v_1 to v.

According to equation 3, k is independent of the units chosen for its expression, except for time. It may be expressed as ml/(cm^2×cm head), or as in.^{3}/(in.^{2}×in. head), filtered per second, or in any other consistent units.

It is apparent from equation 3 that, if the ratio of v_1 to v is kept constant, the time of filtration through a given filter paper should be the same regardless of the volume of water used. In this case, k becomes a very simple function of the time of filtration. For example, if the measurements are so made that $v=1/2v_1$, and t_1 is taken as zero when the volume in the cone is v_1,

$$k=0.3465/t \tag{4}$$

for any value of v_1 that may be chosen. Such a simple relation, together with the simplicity of the method, seems to place the cone method in a very favorable light.

Some illustrative data are shown in tables 1 and 2. In the tests which these data represent, the freely suspended cone of filter paper was first saturated with distilled water and drained, and then 25 ml of the distilled water was poured in all at once. The time was recorded for successive increments of the filtrate collected. The volume remaining in each case was obtained by difference. In table 1 the time in seconds is tabulated against the volume remaining in the cone, at the intervals required to filter 3 ml of water.

In the first part of table 2 are shown values of the water-filtration coefficient, calculated by equation 3, for the intervals of volume change indicated in column 1 of table 1. In the second part of table 2 are shown the values of the coefficient, calculated by equation 4, when the volume in the cone has been reduced by one-half. The coefficient K is 10^4k.

TABLE 1.—*Data obtained by the cone method with six kinds of filter papers*

Volume in cone	Filtering time of sample—					
	1	2	3	4	5	6
ml	*sec*	*sec*	*sec*	*sec*	*sec*	*sec*
25	0	0	0	0	0	0
22	68	31	21	15	7	3
19	137	64	42	31	14	5
16	213	103	67	48	22	7
13	306	150	97	67	31	11
10	407	209	135	89	44	15
7	-------	281	186	120	60	21
4	-------	387	-------	163	88	29

TABLE 2.—*Water-filtration coefficients* [1] *calculated from the data in table 1*

Change in volume		Value of K for sample—					
From	To	1	2	3	4	5	6
ml	*ml*						
25	22	10	21	32	44	95	221
22	19	11	22	34	45	103	361
19	16	11	22	34	50	106	425
16	13	11	22	34	54	115	259
13	10	13	22	35	60	101	328
10	7	----	22	35	58	112	297
7	4	----	23	----	65	100	350
24	12	11	22	35	50	112	347
22	11	11	22	35	52	108	347
20	10	12	22	34	54	105	315
18	9	----	22	35	56	108	389
16	8	----	22	35	57	105	315
14	7	----	22	35	58	105	289
12	6	----	22	33	59	108	315
10	5	----	22	----	61	112	315
8	4	----	22	----	64	105	315

[1] $K=10^4 k$. It may conveniently be thought of as the number of milliliters of water filtered through a square meter of filter paper in 1 second under a head of 1 cm of water.

IV. EFFECT OF CONTINUED FILTRATION ON RATE OF FLOW

Previous work has indicated that the speed of filter paper decreases with time of filtering. Griffin and Parish (see footnote 2) published data showing this effect for a number of filter papers. In one case the speed at the end of 2 hours of continuous filtration had decreased to only 2.5 percent of the value at the beginning. Some further data are given in table 3, which were obtained by the cone method with water not previously filtered. In these tests also the speed decreased progressively as filtration was continued.

TABLE 3.—*Change in speed of filter paper with continued flow of water through specimen*

K, determined after filtering	Water-filtration coefficients [1] for specimen—		
	1	2	[2] 3
ml	K	K	K
0	64	58	53
100	57	47	47
200	50	40	40
500	46	--	--
FILTER REVERSED			
0	71	49	59
100	67	--	54
200	63	41	41

[1] See note under table 2.
[2] Specimen 3 had been soaked for 24 hours before being tested.

Griffin and Parish attribute this effect to "hydration" and swelling of the fibers. Swelling of course takes place, and must have an effect on the speed, at least during the initial stage of filtering, since it makes the paper thicker and affects the size of the pores. Swelling, however, does not seem to explain the change in speed with time of filtering. One of the filter circles reported on in table 3 was soaked for 24 hours before being tested. It behaved very much like the ones not soaked. Continued flow of water through the filter seems necessary to cause slowing of the speed. It is quite possible that swelling and thickening of the paper may make the interstices larger rather than smaller. The data discussed in the next section indicate that the paper probably becomes more permeable to water as a result of swelling.

Lane [4] observed a decrease in permeability of paper with continued flow of oil through it. In this case "hydration" and swelling would be absent or unimportant. He offered as a tentative explanation the orientation of fibers to partially block the flow, but did not consider this explanation altogether satisfactory because an equilibrium state was never reached. Likewise, the slowing of the speed of filter paper seems to go on indefinitely. In one instance during the present investigation, the speed of filtration with distilled water was still decreasing after 7 hours of continuous filtration.

When the flow through filter paper is reversed in direction by refolding the circle, the speed of filtration may be increased temporarily, as the data in table 3 show. It then begins to decrease as before. Lane observed a similar behavior when oil flowed through paper and thought it compatible with the fiber-orientation hypothesis.

Fungoid growths in distilled water have been reported,[5] and it has been suggested that the slowing of the speed of filter paper with time might be explained by the plugging of the pores with such material filtered. There has, however, been no evidence of the operation of this factor during the work reported here.

Muskat [6] observes that a very common cause of the plugging of a porous medium upon continuous flow of liquid through it is the evolution of air or gas dissolved in the liquid. He recommends as a remedy the use of distilled water, and the prefiltering of it before use. Such an explanation seems to be in keeping with many of the observations of the behavior of filter papers. Air bubbles collecting in the pores could explain the decrease of speed with time, even when long-continued; the failure of soaking to slow the speed noticeably; and the behavior of oil flowing through paper (see footnote 4); the temporary increase in the speed of filter paper when the flow of water is reversed in direction; and the fugitive nature of the slowing agent, as indicated by the fact that drying out a filter circle which has exhibited slowing usually restores it to substantially its original speed. This explanation, however, is not consistent with other observations. Boiling the water, or extracting the air by vacuum, does not serve the purpose of prefiltering it. Aerating water that has been prefiltered usually does not cause slowing of the speed of filter paper through which it is filtered.

Simon and Neth,[7] working with filters made of glass, porcelain

[4] Wm. H. Lane, Paper Trade J. 117, TS30 (1943).
[5] A. Griffiths and C. H. Knowles, Proc. Phys. Soc. 24, 350 (1912).
[6] M. Muskat, The Flow of Homogeneous Fluids Through Porous Media, p. 90 (McGraw-Hill Book Company, Inc., New York, N. Y., (1937)).
[7] A. Simon and W. Neth, Z. anorg. allgem. Chem. 168, 221 (1927).

and quartz, found that fresh water (distilled water not previously filtered) or fresh solutions of numerous chemical reagents progressively decreased in rate of filtration when successive portions were passed through the filters. Acetone and carbon tetrachloride behaved in the same way. When they were prefiltered, however, all passed through the filters repeatedly without decrease in rate of filtration. When the prefiltered water, solution, or reagent was boiled or allowed to stand for 1 or 2 days, it again behaved in each instance like fresh (unfiltered) liquid.

They found that a filter that had been clogged or slowed by filtering fresh water through it could be made to filter more rapidly again, either by filtering certain acids through it or by applying an electromotive force (110 or 220 volts) across the filter, provided the negative pole was placed on the discharge side of the filter. They also found that such a filter, clogged by filtering fresh water through it, retained a positively charged colloid while passing a negatively charged colloid of the same particle size, when the two sols were filtered through it.

From their observations they concluded that impurities in the water could not account for the clogging of the filters. They found that air already in the filter is sometimes a factor in its initial behavior, but concluded from experiments made in a vacuum with unfiltered water that air evolved from solution in the water could not be the chief factor involved in clogging the filters.

Simon and Neth concluded finally that a number of complicated factors are responsible for the change in the speed of filters as a result of the passage of liquids through them. Important among these are air already in the filter; order of filtration of various reagents; adsorption of ions; and the electrical condition of the filter and the solution, that is, polarization and potentials produced by flow of liquid through the filter.[8]

Most of the phenomena reported by Simon and Neth pertaining to the behavior of water when filtered through their rigid filters was observed during the present investigation when water was filtered through filter papers. No experiments were made with other liquids.

Whatever may be the cause of the slowing of the speed of filter paper, prefiltering the water consistently improves the behavior and substantially eliminates uncertainty in the test for speed. Using the same portion of water over and over is helpful, since each test prefilters it for the next test.

The effect of prefiltering is illustrated in figure 2. The usual behavior is shown by curve *A* when distilled water not prefiltered is used, fresh portions of the water being filtered through a given circle of filter paper for several successive filterings. Curve *A* is a composite of data for five circles from three kinds of filter papers. The water was from two sources. Sometimes, however, distilled water, not prefiltered, does not decrease the speed of filter paper in this manner. Curve *B* illustrates the behavior when prefiltered water is used. This curve is a composite of the data for 58 circles from 11 kinds of filter papers, obtained with water from three sources. A few of these tests were made with ordinary water from the city supply, after prefiltering it. Such water, not prefiltered, slows the paper much more rapidly than distilled water does. Of the 221 determinations used in arriving

[8] G. H. Bishop, F. Urban, and H. L. White, Colloid Symposium Annual 8, 137 (1930).

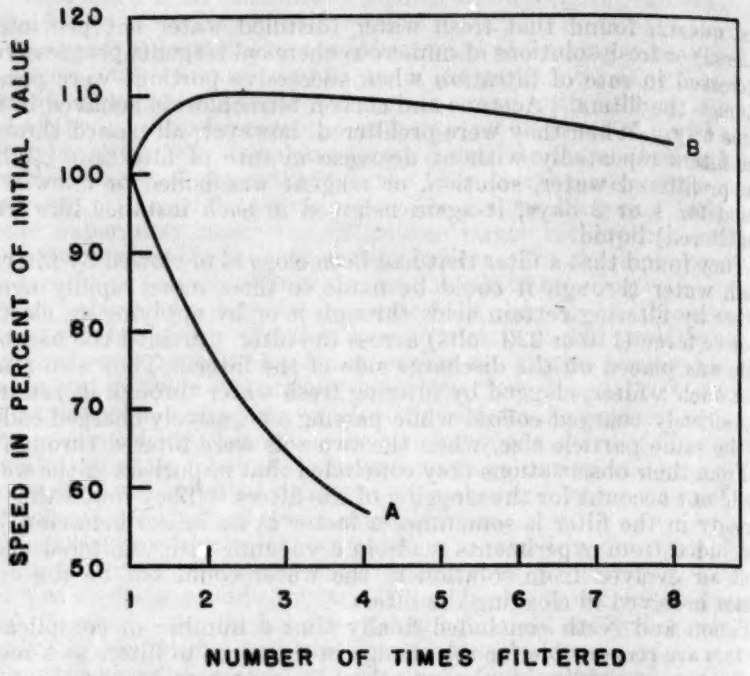

FIGURE 2.—*Change in rate of flow of water through filter paper.*

A, When distilled water is used which has not been prefiltered; and *B*, when prefiltered water is used.

at curve *B*, more than 90 percent were within ±15 percent of this composite curve.

V. RELATION OF AIR PERMEABILITY AND RATE OF FILTRATION

A knowledge of the air permeability of filter papers should be useful in throwing some light on what happens to the structure during filtration, and also in determining the approximate speed of a filter paper before using it.

According to familiar formulations that describe the flow of fluids through a capillary system, the ratio of the rates of flow (in terms of the volumes passing through per unit time, area, and driving pressure) of two fluids through a given capillary system should be equal to the reciprocal of the ratio of their respective viscosities. For air and water at room temperature, air flows through paper about 55 times as fast as water.

The air permeability of a number of filter papers was measured with the Carson [9] instrument. The same specimens were then used in determining the water-filtration coefficient by the cone method. The results are shown in table 4. The ratio varies from 24 to 40, being in all cases considerably less than the theoretical value. If, when filter paper is wet with water, the swelling of the fibers tends to reduce the size of the pores in the paper, as is commonly supposed, the ratio

[9] F. T. Carson, J. Research NBS **26**, 475 (1941) RP1390; see also BS J. Research **12**, 567 (1934) RP661.

in table 4 should be greater than 55 instead of less. It seems likely that the spaces between the fibers become larger as a result of swelling in the structure.

It is observed that in table 4 the papers are arranged in nearly the same order by the two measurements. This fact may be found useful as it affords a means of estimating the speed of filtration without wetting the paper.

TABLE 4.—*Relation of the air permeability of filter paper to the rate of filtration of water*

Sample	Water-filtration coefficient [1] K	Air permeability [1]	Ratio	Sample	Water-filtration coefficient [1] K	Air permeability [1]	Ratio
1	28	680	24	16	175	5,510	32
2	31	835	27	17	220	6,560	30
3	42	1,360	32	18	225	7,330	33
4	55	1,520	28	19	230	6,930	30
5	55	1,680	31	20	230	9,260	40
6	57	1,470	26	21	232	8,690	37
7	60	1,570	26	22	240	7,920	33
8	95	2,510	26	23	272	9,420	34
9	95	3,350	35	24	325	11,200	35
10	107	3,060	29	25	370	12,800	35
11	132	3,540	27	26	415	14,600	35
12	132	4,370	33	27	425	15,600	37
13	140	5,000	36	28	595	20,900	35
14	145	4,730	33	29	615	21,100	34
15	152	4,270	28				

[1] See note under table 2. The air permeability is expressed in the same unit as K.

VI. RECOMMENDED PROCEDURE

The following procedure is recommended for testing the speed of filtration of filter paper. Obtain distilled water (preferably freshly distilled) and prefilter it through filter paper that has a rate of flow at least as slow as that of the paper to be tested. Keep the temperature of the water constant during the tests. A temperature of 23° C is recommended.

Carefully fold a filter circle in the usual way to form a 60-degree cone. Place it in a 60-degree funnel, wet it thoroughly with water prepared in the manner indicated above, and press down the folds to expel all air pockets and to make the three plies smooth and in good contact. Pour out the excess water, remove the cone and suspend it freely over a burette by supporting it in a loop of wire. This loop should be of such a size that it will support the cone at about two-thirds of its height, reckoned from the apex. Immediately, while the cone is saturated with water, pour into the cone all at once a known volume of water which is approximately two-thirds the capacity of the cone. When one-fifth of the water has filtered into the burette, start a stopwatch. When half the remaining volume has filtered through, stop the stopwatch and record the time in seconds. Test 5 to 20 circles, depending on their variability, to obtain an average. Use the same portion of water for each test, adding to it from the prepared supply as found necessary. The average time can be used as an inverse measure of speed, but it is preferable to use the average time as t in the equation $K=10^4k=3465/t$ (eq 4) to obtain a water-filtration coefficient.

The data in table 5 illustrate the application of the method. Each result is the average of five tests.

TABLE 5.—*Data obtained by the recommended procedure*

Diameter of filter circle	Volume poured in	Filter paper *A*		Filter paper *B*	
		Water-filtration		Water-filtration	
		time,[1] *t*	coefficient,[2] *K*	time,[1] *t*	coefficient,[2] *K*
cm	*ml*	*sec*		*sec*	
5.5	3.5	95 ±4.9	36	14 ±2.9	250
7	5	89 ±3.6	39	15 ±1.8	230
9	10	90 ±5.0	39	15 ±1.9	230
11	25	87 ±8.9	40	17 ±3.9	200

[1] Time required to filter half the volume remaining when the stopwatch was started. The limits of uncertainty indicated were calculated by the method recommended in the ASTM Manual on Presentation of Data, Supplement A, for a probability of 9 in 10.
[2] See note under table 2.

WASHINGTON, May 25, 1944

U. S. Department of Commerce National Bureau of Standards

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ATTACK OF REFRACTORY PLATINIFEROUS MATERIALS BY ACID MIXTURES AT ELEVATED TEMPERATURES

By Edward Wichers, William G. Schlecht, and Charles L. Gordon

ABSTRACT

Iridium and other refractory metals and alloys of the platinum group can be easily prepared for analysis, or for small-scale refining, by solution with hydrochloric acid and suitable oxidants in sealed tubes at temperatures up to 300° C. The effects on the rate of solution of iridium caused by variations in temperature, in concentrations of hydrochloric acid and of the oxidant, and in the nature of the oxidant, are reported. The rate increases rapidly with increase in temperature. It also increases with increasing concentration of hydrochloric acid, up to nearly anhydrous hydrogen chloride. With variation in the concentration of chlorine or equivalent oxidants, the rate passes through a maximum at a relatively low concentration.

A number of other factors of less importance are also discussed. Suitable working conditions for dissolving various alloys and minerals are suggested.

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I. INTRODUCTION

Of the six platinum metals only platinum and palladium can be dissolved in aqua regia at temperatures that can be reached in open vessels. The other four and their alloys, such as osmiridium, are nearly unattacked by aqua regia at temperatures up to the boiling point of the acid mixture. In preparing platinum-group minerals for analysis, the customary procedure is to treat them with aqua regia until no more dissolves, and then to worry the undissolved residue more or less completely into soluble form by repeated treatments with alkaline oxidizing fluxes. This process is not only laborious, but may result in losses

of material and in contamination from various sources. Further, the solution eventually obtained contains an undesirable amount of alkali salts. Besides the refractory platiniferous minerals, some manufactured platinum alloys also contain enough rhodium or iridium to make them very difficultly soluble in aqua regia. They are even more difficult to treat by fusion with alkalies.

The stability of the chloro compounds of the platinum metals suggests that the difficulty encountered in dissolving some of the metals in hydrochloric acid plus a suitable oxidizing agent, is not caused by the nature of the reaction but by the rate at which the reaction proceeds at the temperatures ordinarily used. This idea is supported by the fact that a given mass of one of these metals is more rapidly dissolved if the sample is very finely divided, or if the sample of refractory metal is alloyed with a sufficiently large proportion of platinum. In both cases the rate of attack per unit area of exposed surface remains low, but the amount of metal going into solution is increased because the effective surface area is increased. It therefore seemed worthwhile to find out whether the rate of attack could be sufficiently increased for practical purposes at temperatures attainable in glass apparatus.

II. APPARATUS, REAGENTS, AND EXPERIMENTAL PROCEDURE

The pressure developed by concentrated hydrochloric acid or its mixtures with nitric acid or other oxidizing agents increases very rapidly above 100° C. In the observations to be reported, pressures up to 4,000 lb./in.^{2} were often encountered. Well-annealed sealed glass tubes normally will withstand such pressures if the internal diameter is not greater than twice the wall thickness. Pyrex glass tubes of 4-mm diameter and 2-mm wall thickness were used for nearly all the experimental work on rates of solution, with no protection except inclosure in a loosely capped piece of pipe, which served to keep glass from scattering about the oven when an occasional failure occurred. These tubes usually were about 20 cm long. For a few similar experiments, Pyrex tubes of 8-mm bore and 2-mm wall thickness were used. For the solution of minerals and other materials to be prepared for analysis, tubes of 15-mm bore, with about 2.5 mm wall thickness, were used. The latter tubes, also about 20 cm long, were provided with stems of 4- by 8-mm tubing through which the reaction mixture was introduced (fig. 1). The sample was introduced through the neck unless the size of the pieces, such as nuggets of mineral, made it necessary to place them in the larger tube before the stem was sealed on. The reason for using tubes provided with stems of smaller bore has been discussed in a previous paper.[1] In brief, experience showed that the larger tubes could

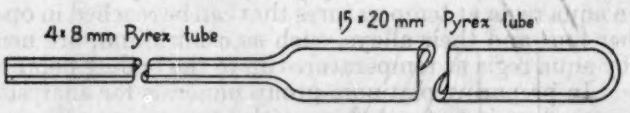

FIGURE 1.—*Sealed tube for solutions.*

The volume of the main tube is approximately 1.77 ml/cm. The tube is made twice the length that will accommodate the desired amount of reacting mixture.

[1] C. L. Gordon, J. Research NBS **30**, 107-111 (1943) RP1521.

not be sealed, after introducing the sample and acid mixture, without leaving the seals so strained as to cause frequent failures at relatively low pressures. Sealing of the stems did not cause trouble of this kind.

An electrically heated oven, suitable for operation at temperatures up to 350° C and thermostatically controlled to 1 degree, was used to heat the apparatus.

For tests of short duration the sealed glass tubes were slid into pieces of pipe, capped at one end, which were lined up in the oven and were at oven temperature. The tubes were thus kept from breaking others of the same series in case of a failure, and the uncertain time lag involved in heating cold pieces of pipe to the temperature of the oven was eliminated.

The larger tubes, if they were to be heated much above 100° C, were enclosed in steel pressure vessels and protected with gas under pressure, as will be described later.

When it was found that rhodium, ruthenium, and osmium were more readily dissolved by suitable acid mixtures than was iridium, this last-named metal was used in studying the effects on the rate of solution of variations in temperature, concentration of hydrochloric acid, and concentration of the oxidizing agent.[2] It seemed entirely probable that conditions suitable for the solution of iridium would result in at least equally rapid attack of any alloy of platinum-group metals, whether a mineral or a manufactured product. Within the range of materials thus far tried, this expectation has been confirmed.

The iridium used for the study of rates of solution was in the form of sheet 0.075 mm thick. The sheet was cut into pieces about 3 by 5 mm, which had a total surface of 30 to 40 mm^2, neglecting the surface area of the edges. The amount of iridium dissolved was determined by weighing the pieces of iridium before and after exposure to the reaction mixtures. The volume of metal dissolved was calculated from the density and the loss in weight. This, in turn, divided by the surface area, yielded the average rate at which the surface was dissolved away during the period of exposure. Rates of solution are expressed in microns per hour. If all surfaces of each particle of metal are attacked simultaneously, the time required for the complete solution of a sample will depend on the thickness (effective diameter) of the largest particle in it, provided that all the particles in the sample are of equally refractory composition.

The periods of exposure of iridium to the reaction mixtures varied from ½ hour to 24 hours. Within this range they were made as long as possible without risking perforation of the iridium sheet, which would have altered the total area too much. This variation in the period of exposure helped to keep the total amount of reaction more nearly constant and thus to minimize the effect of changes in composition of the reaction mixture. The shorter periods were subject to some uncertainty because the time required to bring the reaction vessel to the desired temperature was not precisely known. Tests on tubes containing small amounts of various substances of known melting points showed that tubes slid into a pipe preheated in the oven reached a temperature within 1° C of the oven temperature in 10 minutes.

[2] Although the pressures existing during the experimental work varied greatly, they are discounted from further discussion with the notation that the concentration of the components and the temperature of the system determine the pressure attained, since the volume is fixed. The pressure coefficients of reaction rates are usually very small, hence pressure variations as such were assumed not to affect the rates of attack significantly.

The 4-mm tubes used for the observations on rates of attack had a capacity of about 2 ml. In most of the experiments 1 ml of reaction mixture was used, but in some of those dealing with variations in the concentration of hydrochloric acid the volume was smaller. With these exceptions, which will be noted, variations in results from failure to keep constant the starting ratio of the volumes of the liquid and gas phases are believed to be smaller than those arising from uncontrolled variations in the composition of the reaction systems. In order to determine the change in the volumes of the liquid and gas phases as the temperature rose, one tube, half-filled with a mixture of 1 volume of fuming nitric acid (91 weight-percent of HNO_3) and 20 volumes of hydrochloric acid (36 weight-percent of HCl), was suspended within a heater made by winding resistance wire on a larger glass tube. The maximum increase in volume of the liquid was about 4 percent, at about 300° C. Above that temperature the liquid decreased in volume. At about 390° C the meniscus disappeared, and other phenomena associated with the critical temperature were observed.

In many instances a measured volume (usually 1 ml) of acid mixture was transferred to the reaction tube by means of a pipet. In some experiments in which the composition of the reaction mixture was more closely controlled, the components were added by weight. To do this with chlorine and with hydrochloric acid mixtures prepared from water and hydrogen chloride, it was necessary to chill the tubes to the temperature at which the gases would liquefy. In such instances the tubes to be charged were cooled by a slush of carbon dioxide in a mixture of equal volumes of chloroform and carbon tetrachloride. For the condensation of dry hydrogen chloride gas, liquid air was tried as a direct coolant but its temperature was too far below the freezing temperature of hydrogen chloride (−111°C) and only a snow, which plugged the small tubes used, could be obtained. Dry ice in ether, through which air is bubbled, was found to have an equilibrium temperature of −95° C and hence 10° C below the temperature of condensation of hydrogen chloride. The fire hazards involved in sealing tubes over this mixture may be avoided by transferring the tube, after it is charged, to liquid air.

With this method of charging the tubes, chlorine and hydrogen chloride could not be added in the exact amounts desired. Instead, several mixtures were made so that the ratios would be in the desired range. The tubes were charged and then sealed by heating the open end until the glass flowed together, after which slight warming of the tube below the seal caused the seal to blow out into the desired rounded shape. This procedure made it possible to determine by gain in weight the amount of the volatile component which had been added.

The reactions by which metallic iridium is changed to a soluble chloride may be represented by the single reaction,

$$Ir+4Cl+2Cl^-\rightarrow IrCl_6^{=}.$$

To be dissolved, iridium must both be oxidized and be converted into the chloroiridate ion. The chloroiridite ion, $IrCl_6^{\equiv}$, is another possible soluble form but does not appear as long as chlorine or an equivalent oxidant is present in excess. Chlorine in the presence of hydrochloric acid is an effective oxidant for iridium at temperatures from 250° to 300° C; in fact, the results of the present work show it to be just as effective as mixtures of hydrochloric acid with nitric acid, or

with perchloric acid, of equal stoichiometric oxidizing power.[3] Consequently, the latter reagents will be regarded merely as sources of chlorine, in accordance with the reactions,

$$7HCl + HClO_4 \rightarrow 4Cl_2 + 4H_2O$$

$$10HCl + 2HNO_3 \rightarrow 5Cl_2 + N_2 + 6H_2O$$

The reaction between hydrochloric acid and perchloric acid is far from instantaneous, even at 300°, but the indicated products are the only ones that can be reasonably expected. The expression given for the reaction between hydrochloric acid and nitric acid is justified by an experiment in which an excess of finely divided iridium was heated at 300° for 120 hours with a mixture of 20 volumes of hydrochloric acid and 1 volume of fuming nitric acid. In the resulting solution, no evidence was found of oxides of nitrogen, or of the ammonium radical or hydroxylamine. The pressure within the tube when opened at room temperature suggested the presence of nitrogen. Stoichiometric calculations indicated the stage of valence of the nitrogen to be not higher than zero. In this instance, with the oxidant entirely consumed, the dissolved iridium was partly in the form of $IrCl_6^{\equiv}$ and partly in the form of $IrCl_6^{=}$ ions.

Sodium chlorate was also used as an oxidant largely because it could be added conveniently as weighed amounts of the crystals. Its reaction with hydrochloric acid to form chlorine is very rapid, even at room temperature. Consequently, the acid in the tube had to be frozen before the chlorate was introduced.

The small variations in the ratio of the volume of liquid to that of vapor in the tubes, with consequent changes in the composition of the two phases, have already been mentioned. When temperature was the variable under consideration, the composition of both phases also varied considerably because of the changing partial vapor pressures of the components and because of the changing density of the liquid. The composition of the system varied further as the reaction proceeded, and to different extents if the total amount of reaction was not constant. At the optimum concentrations of chlorine a large part of the total amount of chlorine present was consumed in the reaction. On the other hand, the concentration of hydrogen chloride, which was always large relative to the amount of chloride ions consumed, was little affected.

When sodium chlorate was used as the oxidant, sodium chloride was present as an additional component. It should also be pointed out that the tubes contained about 1 ml of air at atmospheric pressure. To the oxygen from this source must have been added some produced by the reaction between chlorine and water at the elevated temperatures. Finally, the formation of chloroiridate ions during the reaction introduced still another component into the system. For all these reasons the systems were much too complicated to permit considering the observed rates of attack as in any sense characteristic of completely defined systems. Instead, they were considered only as having relative significance and as pointing the way to combinations of temperature and composition of the acid mixtures that could be used to get optimum rates of solution for the practical purposes of chemical operations.

[3] In the case of platinum, molecular chlorine in the presence of hydrochloric acid does not appreciably attack the metal at temperatures up to 100° C., whereas the familiar aqua regia does so readily, as do also mixtures of hydrochloric acid with certain oxidants other than nitric acid, even ferric chloride.

III. EXPERIMENTAL RESULTS

1. EFFECT OF VARIATION IN TEMPERATURE

Preliminary experiments showed that mixtures containing a much smaller proportion of nitric acid than that commonly used in aqua regia (3 or 4 volumes of hydrochloric acid to 1 of nitric acid) were much more effective than aqua regia in dissolving iridium at elevated temperatures. A mixture of 20 volumes of concentrated hydrochloric acid (about 36 weight-percent of HCl) with 1 volume of fuming nitric acid (about 91 weight-percent of HNO_3) was used in many of the experiments in which nitric acid was the oxidant. With this mixture, the rate of solution of iridium was 0.05 micron per hour at 225° C. Above this the rate of attack increased rapidly with rising temperature. At 255° C the observed rate was 0.44; at 275° C, 1.3; and at 300° C, 2.2 microns per hour. Above 300° C there was some conflict in the evidence about a continuing increase in rate of attack. Since 300° C was the maximum temperature that was convenient for operation with the facilities at hand, and since it was found to provide an adequate rate of attack by suitably chosen reaction mixtures, no detailed study was made of reaction rates at higher temperatures. From the figures given for the interval from 225° to 300° C it will be seen that the variation of rate with temperature is similar to that observed for chemical reactions in general. Supporting evidence was obtained in two series of experiments, one at 250° and one at 300° C, in which the variable under study in each series was the concentration of chlorine. For comparable concentrations of chlorine the rate at 300° C was four or more times that at 250° C.

2. EFFECT OF VARIATION IN THE CONCENTRATION OF HYDROGEN CHLORIDE

In a preliminary series of observations at 260° C the ratio of 1 volume of fuming nitric acid to 20 volumes of hydrochloric acid was maintained, but the strength of the hydrochloric acid was varied from 27 to 45 weight-percent of HCl. This was done by mixing ordinary concentrated hydrochloric acid, which contains 35 to 36 weight-percent of HCl, with water or with varying amounts of a fortified acid (45 weight-percent of HCl), which was prepared by fractionally distilling the ordinary acid and collecting the first fractions in a chilled receiver. The rates of attack observed with mixtures containing 27 and 36 weight-percent of HCl were one-fifth and one-half, respectively, of that observed with acid containing 35 weight-percent of HCl. With mixtures containing 40 and 45 weight-percent of HCl the rates were respectively, 5 and 8 times that of the solution containing 35 weight-percent of HCl.

The total range in relative rates for these variations in strength of added hydrogen chloride was thus 1 to 40. If all of the nitric acid added is assumed to react with hydrochloric acid to yield water, chlorine, and nitrogen, there is a drastic change in the effective concentration of hydrochloric acid in the mixture. On this assumption the concentration of hydrogen chloride changes from 27 to 11, from 35 to 21, and from 45 to 34 weight-percent of HCl. On this basis the extreme range in final concentration of the acid, as weight-percent of HCl, is from 11 to 34, which corresponds to a threefold difference instead of from 27 to 45, in which the strongest acid is less than

twice as concentrated as the weakest. When this work was done, the rates were not calculated in microns per hour, hence the results are comparable only among themselves and not with those observed in other series of experiments.

Several other series of observations were made in which 0.050 g of sodium chlorate was used as the oxidizing agent instead of 0.05 ml of fuming nitric acid. This amount of sodium chlorate yields 0.100 g of

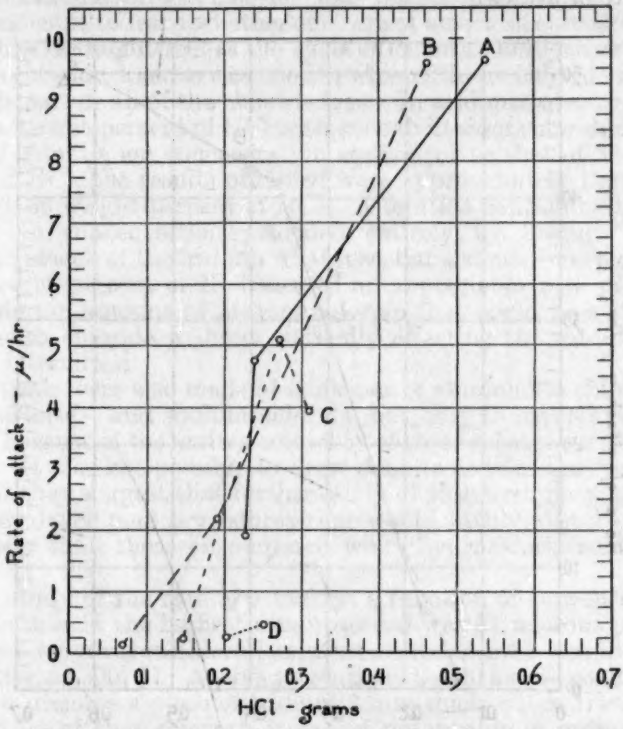

FIGURE 2.—*Effect of the amount of hydrogen chloride present after reaction with 0.05 g of* $NaClO_3$ *on the rate of solution of iridium at approximately 250° C.*

[On page 369 is given a tabulation of the conditions under which the data were obtained]

chlorine by reaction with hydrochloric acid. The reaction mixtures were prepared in each tube by measuring or weighing-in definite amounts of water, chlorate, and hydrogen chloride. The results obtained at approximately 250° C are shown in figure 2. In this figure the concentration is given in terms of the effective hydrogen chloride, that is, the weight of added hydrogen chloride corrected for that used to produce chlorine by reaction with sodium chlorate. The following are the conditions under which these observations were made.

Group	H_2O	Temperature	Duration of experiment
	g	*°C*	*hr*
A	0.10	250	1
B	.10	245	2
C	.20	245	2
D	.50	250	1

The conditions under which the results of groups *A* and *B* were obtained can be considered substantially identical. The relatively close agreement of the results of group *C* with those in *A* and *B* indicate that the ratio of hydrogen chloride to water is much less important than the absolute concentration of hydrogen chloride. However, the two results in group *D*, obtained with a much different ratio of hydrogen chloride to water, show that the relative concentration has some bearing on the rate of attack.

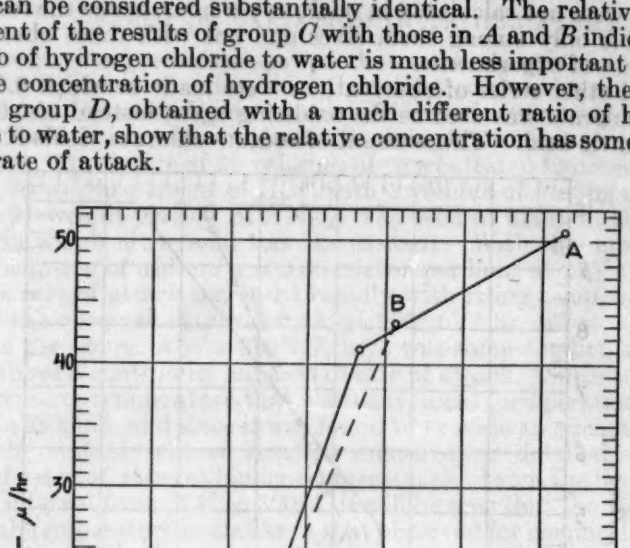

FIGURE 3.—*Effect of the amount of hydrogen chloride after reaction with 0.05 g of* $NaClO_3$ *on the rate of solution of iridium at 300° C.*

Total time ½ hr. Amount of H_2O: Curve *A*, 0.1 g; curve *B*, 0.2 g.

Figure 3 shows results obtained at 300° C. The concentration of acid is again expressed as the effective weight of hydrogen chloride in the system at the beginning of the period. Figure 3 shows that the rate of attack at 300° C increases rapidly with increasing hydrogen chloride content. Comparison with figure 2 shows that the change of rate is about 5 times as great at 300° as at 250° C, as described in a previous section. The variation in the ratio of hydrogen chloride to water in the two sets of data is substantially without effect.

The data in figure 3 suggests that if the ratio of hydrogen chloride to water exceeds 4 or 5 to 1, the effect of increasing absolute concentration of hydrogen chloride falls off. This was borne out by four trials with iridium sheet in which an attempt was made to have present only hydrogen chloride and chlorine, but, in two of the experiments, traces of

water were accidently introduced. These two showed slightly higher rates than the two in which water was thought to be absent, but the rates for the entire series were very low. They ranged from 0.008 to 0.3 micron per hour. It is quite evident that some water must be present for the reaction to proceed at an appreciable rate. It appears that the presence of moderate amounts of water does not appreciably affect the rate; but there are indications that too much water, that is, more water than hydrogen chloride, may reduce the rate.

In an attempt to learn whether the rate of attack observed with hydrogen chloride might reflect the effect of chloride ions rather than of hydrogen chloride, a series was tried in which lithium chloride was used to provide part or all of the chloride ions. In acid mixtures containing 15 and 21 weight-percent of HCl with enough lithium chloride added to make the chloride ion concentration equivalent to that of 36 weight-percent of HCl, the results obtained were approximately the same as those with 36 weight-percent of HCl. A solution containing the same chloride ion concentration provided entirely by lithium chloride showed no attack of the iridium whatever, but a similar one containing 1 to 2 weight-percent of HCl showed an appreciable rate of attack. The maximum amount of lithium chloride that could be substituted for hydrogen chloride without markedly affecting the rate of attack was not determined.

A few trials were also made of additions of ammonium chloride, potassium chloride, and sodium chloride, but only in moderately small amounts because of the limited solubility of these substances in the acid mixture. It was not possible to draw definite conclusions from these trials, but they suggest that further study of such systems might be of interest in developing procedures that would involve total pressures much lower than those encountered when hydrochloric acid is used alone.

In the study of the rate of attack as a function of concentration of hydrochloric acid the highest rate observed was 51 microns per hour, with a water-hydrogen chloride mixture containing 84 weight-percent of the latter, at 300° C. At this rate a period of 20 hours would be long enough to dissolve a piece of iridium 2 mm thick. It is true that an acid mixture of that strength is hardly practicable in ordinary analytical work. On the other hand, the liquid-vapor ratio was considerably below the optimum. Likewise, the chlorine concentration (0.1 g of chlorine per ml of acid) was much higher than the optimum, as will be shown in the next section. By proper selection of conditions, rates of at least 25 microns per hour can be attained without the use of fortified hydrochloric acid.

3. VARIATION IN THE CONCENTRATION OF CHLORINE

It has already been noted that a mixture of one volume of fuming nitric acid (91 weight-percent of HNO_3) with 20 volumes of hydrochloric acid (36 weight-percent of HCl) was found to attack iridium much more rapidly than the usual aqua regia mixture. The mixture containing the smaller proportion of nitric acid dissolved iridium 20 times as fast as did ordinary aqua regia. When the ratio of nitric acid to hydrochloric acid was further decreased, to 1:40, the rate of attack again increased, by a factor of 3. A partial explanation lies in the fact that the reaction between the two acids at the high temper-

atures of the experiments results in an increase in the amount of water in the system (in proportion to the amount of oxidant added) and a corresponding decrease in the amount of hydrogen chloride. Hence, the loss in concentration of the hydrochloric acid is less with the smaller proportion of oxidant. If the reaction yields water, chlorine, and nitrogen, the strength of the hydrochloric acid in the 1:20 and 1:40 mixtures mentioned above can be regarded as changing from an initial concentration of 36 weight-percent of HCl to 20 and 28, respectively.

Later experiments, in which chlorine, as such, was used as the oxidant, thus maintaining a constant amount of hydrogen chloride in the system except for the small amount consumed by the formation of $IrCl_6^{=}$ ions, showed that the rate of attack varied markedly as a function of the concentration of chlorine.[4] Four groups of these

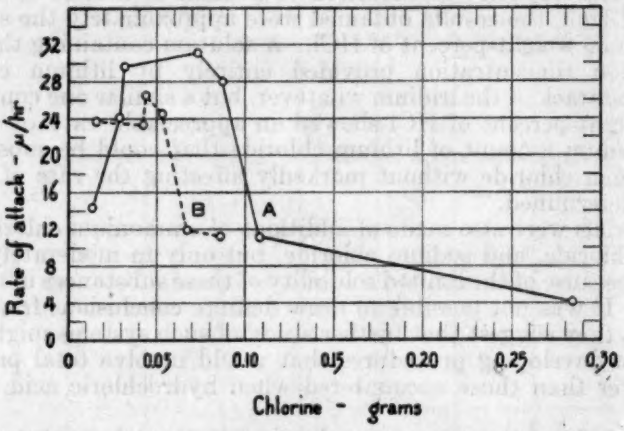

FIGURE 4.—*Effect of the amount of chlorine on the rate of solution of iridium in 1 ml of 36 weight-percent of* HCl *at 300° C.*

Curve *A*, for 1 hr; curve *B*, for ½ hr.

observations are shown in figures 4 and 5. In the experiments recorded in figure 4, the conditions kept constant were the quantity of hydrochloric acid and the temperature. The three higher rates shown in series *A* are lower than the true values for the corresponding concentrations of chlorine because the pieces of iridium were nearly destroyed, with a consequent marked decrease in surface area toward the end of the period of attack.

Figure 5 shows two sets of results obtained with 1 ml of acid in a 2-ml tube, heated for one-half hour at 300° C. Chlorine, *A*, and sodium chlorate, *B*, were used as the oxidants. The strength of the hydrochloric acid, after allowing for that consumed by the reactions with chlorate, was 28 weight-percent (corresponding to 0.35 g of HCl in the system). To correlate these results with the preliminary observations on varying amounts of nitric acid it should be pointed out that 1 ml of a 1:40 mixture of hydrochloric-nitric acid would contain the equivalent of 0.1 g of chlorine. Thus, the results obtained previously with that mixture should correspond approximately to those obtained with the largest concentration of chlorine shown in figure 5. Although the

[4] Although the chlorine formed a separate liquid phase in these systems at room temperature the extra phase disappeared much below 300°C.

variations shown in figures 4 and 5 are not as regular as might be desired, it appears that, beginning with very low concentrations, there is at first a rapid increase in the rate of solution to a fairly well-defined maximum, after which the rate declines sharply at first and then more gradually. The same behavior is shown in figure 6, in which are given the results of a group of observations similar to the others, except that the temperature was 250° C. The period was 1 hour. The oxidant

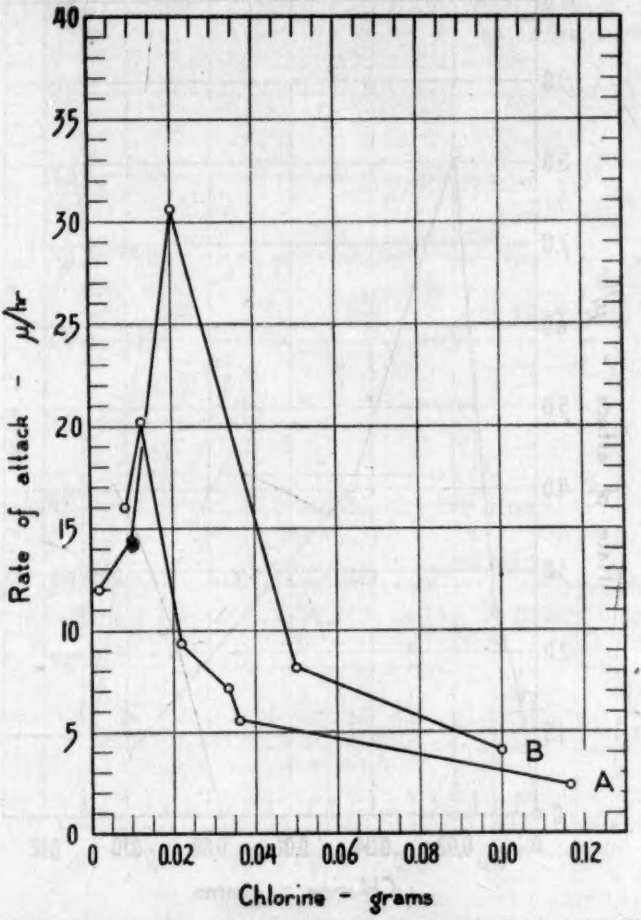

FIGURE 5.—*Effect of the amount of chlorine on the rate of solution of iridium with constant concentration of* HCl *when heated ½ hour at 300° C.*

Curves, *A*, 1 ml of 28 weight-percent HCl with added chlorine; *B*, solution equivalent to *A*, but with the chlorine supplied by additions of $NaClO_3$.

was sodium chlorate. In this group the net hydrogen chloride content of the acid varied, because no adjustment was made for the acid used by reaction with chlorate, from 36 weight-percent for the lowest concentration of chlorine to 28 weight-percent for the highest. In this series sodium chloride was added in varying amounts so that the total sodium chloride content, taking into account that yielded by the sodium chlorate, was constant. This was done to obviate any possible effect of changes in the concentration of this component.

A few experiments were performed with perchloric acid as the oxidant. In this system, and in the nitric acid-hydrochloric acid system, all the oxidant is not immediately available as chlorine. Consequently, the variation in rate of attack with varying concentration of oxidant is not directly comparable with the results obtained with chlorine and with sodium chlorate.

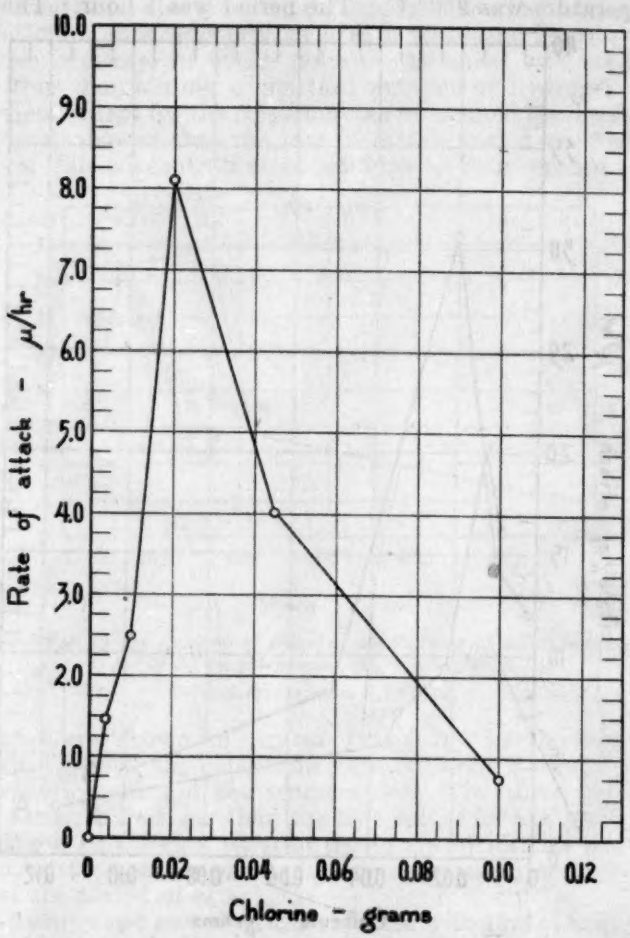

FIGURE 6.—*Effect of the amount of chlorine, produced from sodium chlorate, on the rate of solution of iridium, in 1 ml of 36 weight-percent* HCl, *when heated 1 hour at 250° C.*

The amount of chlorine consumed by reaction with iridium at low concentrations of chlorine caused a change in its concentration, since the iridium surface was large compared with the amount of reaction mixture. In figure 6, for example, in the experiment that gave the highest rate, the amount of chlorine left at the end of the reaction period was 0.017 g, as against 0.020 g at the beginning of the period. The results of similar experiments in tubes of larger capacity, where the volume of reaction mixture was five times as great, but with the

same area of iridium and the same concentration of chlorine in the reaction mixture, are shown by curves *B* and *C* in figure 7.

Figures 4 to 7, inclusive, show that careful attention must be given to the concentration of chlorine in determining the optimum conditions for the solution of iridium. These figures indicate that the optimum concentration is in the range 0.02 to 0.04 g of chlorine per

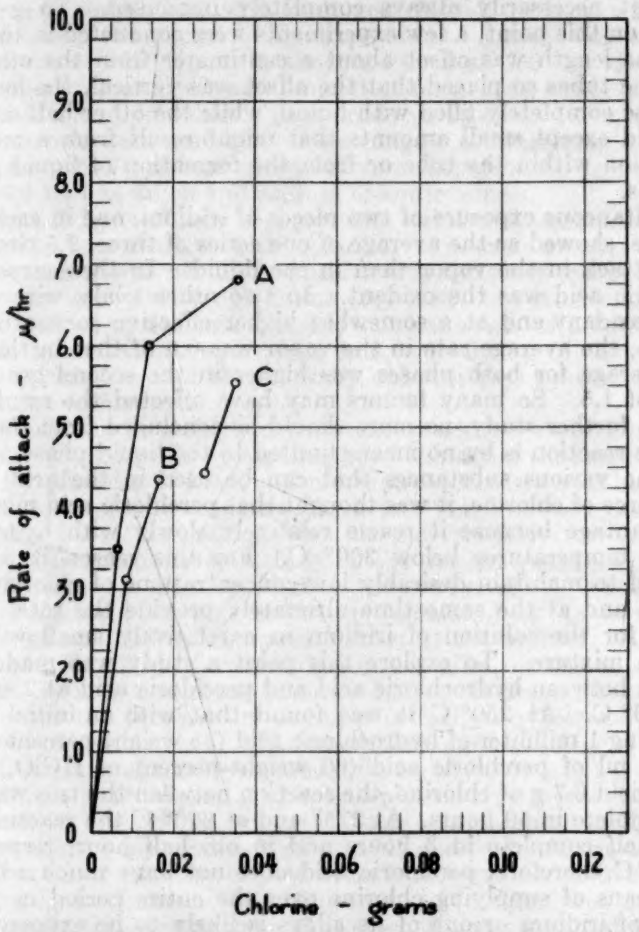

FIGURE 7.—*Comparison of the initial rates of solution of iridium at the lower concentrations of oxidant with larger amounts of reaction mixture.*

A, Volume of solution used was 1 ml of 36 weight-percent HCl plus the chlorine. Heated 1 hour at 250° C; *B*, volume of solution used was 5 ml 36 weight-percent of HCl plus the chlorine. Heated 1 hour at 251° C; *C*, volume of solution used was 5 ml 36 weight-percent of HCl plus the chlorine. Heated 2 hours at 251° C. For comparison with other curves, the amounts of chlorine used in obtaining curves *B* and *C* have been divided by 5 and plotted as the grams of chlorine per 2 ml capacity of reaction chamber.

milliliter of hydrochloric acid. If an initial concentration of 0.04 g/ml is used, the amount of reaction mixture should be adjusted to the amount of iridium to be dissolved, so that the final concentration of chlorine will not be much less than 0.02 g/ml.

4. MISCELLANEOUS OBSERVATIONS

In view of what has been said earlier about variation of composition in the liquid and gas phases, it may be of interest to note that the reaction should not be considered as occurring in the liquid phase only. The reaction tubes were placed in the oven horizontally, but since they were never more than half full of liquid the pieces of iridium were not necessarily always completely immersed. To get information on this point, a few experiments were conducted in tubes half of whose length was offset about a centimeter from the other half. With the tubes so placed that the offset was vertical, the lower half would be completely filled with liquid, while the other half contained no liquid except small amounts that might result from a process of distillation within the tube or from the formation of liquid reaction products.

Simultaneous exposure of two pieces of iridium, one in each end of the tube, showed as the average of one series of three, 2.5 times more rapid attack in the vapor than in the liquid. In these experiments perchloric acid was the oxidant. In two other trials, with chlorine as the oxidant and at a somewhat higher effective concentration of chlorine, the average rate in the vapor was 0.6 of that in the liquid. The average for both phases was higher in the second group by a factor of 1.5. So many factors may have affected the results that, without further study, no more should be concluded from them than that the reaction is by no means limited to the liquid phase.

Of the various substances that can be used in the acid mixture as a source of chlorine, it was thought that perchloric acid might have an advantage because it reacts relatively slowly with hydrochloric acid at temperatures below 300° C. For this reason it might be expected to maintain desirably low concentrations of chlorine in the mixture and at the same time ultimately provide the total amount needed for the solution of iridium in a relatively small volume of reaction mixture. To explore this point a study was made of the reaction between hydrochloric acid and perchloric acid at 250°, 275°, and 300° C. At 250° C it was found that with an initial mixture containing 1 milliliter of hydrochloric acid (36 weight-percent of HCl) and 0.1 ml of perchloric acid (60 weight-percent of $HClO_4$), which would yield 0.7 g of chlorine, the reaction between the two was about half complete in 40 hours. At 275° and at 300° C the reactions were about half complete in 3 hours and in one-half hour, respectively. At 300° C, therefore, perchloric acid does not have much advantage as a means of supplying chlorine over the entire period in which a sample of iridium or one of its alloys is likely to be exposed to the reaction mixture. At lower temperatures it may be expected to act in the desired manner, unless its reaction with hydrochloric acid is catalyzed by the iridium or the reaction products. It has the very real advantage of not reacting at all with hydrochloric acid at room temperature. Thus it can be added to hydrochloric acid without making it necessary to chill the tube before sealing, as must be done if sodium chlorate or chlorine is added. Tubes containing nitric acid and hydrochloric acid in the proportion suitable for this work can be sealed without chilling. However, nitric acid may possibly have a specific disadvantage because of its tendency to introduce nitroso

groups into the chloro complexes of certain platinum metals, notably ruthenium.

A few trials of hydrogen peroxide as the oxidant suggested that it also acted as a source of chlorine by reaction with hydrochloric acid, but the rate of attack on iridium was less than was obtained with other sources of chlorine. It is possible that some of the peroxide dissociates to form water and oxygen and that the oxygen does not in turn come to equilibrium with hydrogen chloride to form water and chlorine during the period of the experiment. In one instance this was 16 hours at 250° C and in another 1 hour at 300° C. Hydrogen peroxide has further disadvantages in that, for a given yield of chlorine, its reaction with hydrochloric acid produces twice as much water as does perchloric acid, and that the strongest commercially available reagent contains 70 percent of water, whereas perchloric acid contains only about half as much and sodium chlorate none.

Bromine, in hydrochloric acid solution, was found to attack iridium considerably less readily than chlorine. An even smaller rate of attack by iodine was not distinguished with certainty from that produced by the air present. So far as they went, the experiments with bromine seemed to indicate a nearly constant rate of attack over a range of concentrations equivalent to 0.05 to 0.20 g of chlorine, the range in which the rate of attack by chlorine rapidly declines with increasing concentration.

Ferric chloride, in a single experiment, produced a significant rate of attack. Experiments by McCaughey [5] show that the rate of attack on gold by solutions of ferric and cupric salts increased with increasing concentrations of the oxidants (in a low range of concentrations). This might be of interest, in view of the relatively low oxidation potential of ferric chloride, in studying the mechanism of the reaction by which iridium is dissolved, but it was not further explored.

Oxygen (other than that in the air remaining in the tubes after sealing) was not used in this investigation as the oxidant. However, Tronev and Bondin [6 7] have made some studies on the solution of platinum, iridium, and rhodium under higher air pressures. In their investigation the increase of pressure is really an increase in concentration of the oxidant. The maximum amount they used was stoichiometrically equivalent to about 0.04 g of chlorine in a 2-ml tube.

Bromine in hydrobromic acid solution (48 weight-percent of HBr) was also tried, but the rate of attack was considerably less than that with equivalent concentrations of chlorine and hydrochloric acid. In one trial, a small quantity of potassium iodide was added to a system containing hydrochloric acid and chlorine, but no significant effect was produced. In this system the end product is a compound of trivalent iridium rather than of the quadrivalent metal. There is no apparent advantage gained by substituting bromo- or iodo-complexes for the chloroiridate ion as the end product of the reaction.

5. PREPARATION OF SAMPLES FOR ANALYSIS

Among the materials on hand suitable for practical trials of the new procedure was a granular, impure iridium containing particles up to

[5] W. J. McCaughey, J. Am. Chem. Soc. **31**, 1261-70 (1909).
[6] V. G. Tronev, and S. M. Bondin, Ann. secteur platine, Inst. chim. gén. (USSR) **15**, 113-23 (1938).
[7] V. G. Tronev, Compt. rend. acad. sci. URSS **15**, 555-8 (1937) in German. A résumé of the preceding reference.

nearly a millimeter thick. This material has the interesting history of having been recovered over a considerable period of time from the anode residues obtained during the electrolytic refining of gold in the United States Assay Office at New York. It contains some ruthenium but virtually no other platinum metals. To get it into solution for analysis would ordinarily pose a difficult problem. During the early trials of the procedure 1.5 g of this material was attacked with 15 ml of a fortified hydrochloric acid (47-48 weight–percent of HCl) and 0.75 ml of fuming nitric acid (91 weight-percent of HNO_3). This was done in a 15-mm Pyrex tube protected by a compensating pressure of 3,500 to 4,000 lb/in.^{2} in a steel shell. After heating for 24 hours at 300° C a few undissolved grains were still visible. After the tube was heated 2 days longer at 300° C there was left one tiny grain of metal and a few grains of sandy, nonmetallic material. Although the fortified hydrochloric acid in this early trial was favorable to a rapid rate of attack, the quantity of nitric acid used was very much larger than the optimum.

A 2-g sample of the same material was heated at 300° C with 20 ml of hydrochloric acid (36 weight-percent of HCl) and about 2 g of chlorine. After 24 hours there was a small residue. In this instance also the amount of oxidant used was too large.

Samples of about 1.5 g of a coarse-grained California mineral, which subsequent analysis showed to contain approximately equal amounts of iridium, osmium, ruthenium, and platinum (with minor amounts of rhodium and iron), were treated with 20 ml of hydrochloric acid (36 weight-percent of HCl) and 1 g of sodium chlorate (equivalent to 2 g of chlorine) at 300° C for 24 hours. Solution was complete. Nuggets of an Alaskan mineral high in iridium, weighing from 1.1 to 1.6 g, also were completely dissolved in a mixture of 15 ml of hydrochloric acid (36 weight-percent of HCl) and 0.4 to 0.7 ml of a solution of 60 weight-percent of perchloric acid when heated at 300° C for 24 hours.

In this laboratory the mixture commonly used to dissolve ordinary platinum in open vessels consists of 4 volumes of hydrochloric acid (36 weight-percent of HCl), 1 volume of water, and 1 volume of nitric acid (70 weight-percent of HNO_3).[8] This is not the most favorable mixture for use in sealed vessels at about 100° C as will be seen from table 1. A companion experiment, in which a mixture of 1 ml of

TABLE 1.—*Rates of attack of pure platinum at 100° C with different mixtures of hydrochloric and nitric acid*

Acid mixture, parts by volume			Rate of attack
HCl	HNO_3 [a]	H_2O	
			Microns/hr
4	1	1	100
4	1	-----	157
8	1	-----	167
20	1	-----	119
100	1	-----	26

[a] The nitric acid used in the first mixture was the ordinary acid (70 weight-percent of HNO_3). In the others, fuming acid (91 weight-percent of HNO_3) was used.

[8] This mixture, which involves slight dilution with water, has very nearly the hydrogen chloride concentration of constant-boiling hydrochloric acid and hence is more economical to use on a large scale than the undiluted mixture.

hydrochloric acid and 0.05 g of sodium chlorate was used, showed a rate of attack of 167 microns per hour.

Platinum alloyed with as little as 10 percent of iridium is dissolved only slowly by aqua regia in open vessels at the temperature of the steam bath. In the course of analyzing a large number of samples of platinum-iridium alloys it has been found very useful to seal the samples (weighing about 0.5 g and in the form of chips 0.1 to 0.2 mm thick) in 8-mm tubes with 5 ml of a mixture of 8 to 10 volumes of hydrochloric acid and 1 volume of nitric acid. When the tubes are heated overnight at about 110° C, solution is accomplished with a minimum of inconvenience. At 110° C tubes of this size, of standard wall thickness, need no external protection.

IV. BEST OPERATING CONDITIONS

On the basis of the foregoing discussion and of other experience in this laboratory, recommendations can be made as to desirable conditions for the solution of refractory platiniferous materials in hydrochloric acid mixtures at elevated temperatures. By a suitable choice of conditions, samples to be analyzed can be converted into a solution of chloro-compounds in a small volume of acid, without contamination, without loss of volatile reaction products such as osmium tetroxide, and without the use of unusual equipment other than the steel shell in which the larger tubes must be placed to protect them against excessive internal pressures.

1. QUANTITY AND STRENGTH OF HYDROCHLORIC ACID

For most materials ordinary concentrated hydrochloric acid (about 36 weight-percent of HCl) is satisfactory. For unusually large particles or for exceptionally refractory materials it is desirable to use a stronger acid. Concentrations up to about 50 weight-percent of HCl are conveniently prepared by distilling some of the ordinary acid through a condenser cooled with very cold water into a receiver packed in ice. Ratios of hydrogen chloride to water, higher than 1 to 1, can be prepared by condensing dry hydrogen chloride on top of frozen water. The amount of acid used must be sufficient to produce the best ratio of acid to oxidant which is 20 g of HCl to 1 g of Cl_2.

Not less than 4.2 g of HCl should be used for each gram of sample. If ordinary acid is used, 10 ml of acid per g of sample is the minimum. A larger quantity, up to 20 ml per g , will hasten complete solution.

2. NATURE AND QUANTITY OF OXIDIZING AGENT

The best quantity of oxidizing agent for the solution of iridium at 250° to 300° C is 0.025 g of Cl_2 per milliliter of internal tube volume, provided as chlorine or by the action of any chlorine-producing oxidant.

Perchloric acid,[9] preferably of 70 weight-percent, is the most convenient oxidant to use if the reaction is to be conducted at temperatures above 250° C. At lower temperatures it reacts too slowly with hydrochloric acid to be suitable, and nitric acid or sodium chlorate should be used instead, the latter only if there is some reason to avoid the

[9] WARNING.—If organic matter is present there is danger of explosion by reaction with the perchloric acid.

possible formation of nitroso compounds, such as $(RuNOCl_5)^=$. For each gram of sample consisting predominantly of iridium, osmium, or platinum, 0.22 ml of perchloric acid of 70 weight-percent of $HClO_4$ should be used. If nitric acid is used as the oxidant, 0.27 ml of the ordinary acid (70 weight-percent of HNO_3) or 0.19 ml of the fuming acid (91 weight-percent of HNO_3) corresponds to the 0.22 ml of perchloric acid solution. The corresponding weight of sodium chlorate is 0.37 g. If the sample contains significant amounts of rhodium or ruthenium, a larger amount of oxidant should be used, in proportion to the smaller equivalent weight of these metals. It should be noted that if perchloric acid is used at temperatures much below 300° some of it is likely to remain if the period of heating is not over 24 hours. Its presence may be undesirable in later analytical operations; for example, osmium or ruthenium tetroxide may be evolved if the solution is evaporated by heating.

For iridio-platinum alloys, which can be dissolved at temperatures as low as 100° to 150° C, perchloric acid is not recommended. For these alloys about 0.27 ml of nitric acid (70 weight-percent of HNO_3) per g of metal is desirable, or sodium chlorate, 0.37 g per g of metal, can be substituted.

3. TEMPERATURE

In general, the temperature at which the reaction is conducted should be no higher than is necessary to get complete solution in a convenient length of time, for example, in 18 to 24 hours. Temperatures as high as 300° C will be needed for only the most refractory materials, unless the sample particles are unusually large. Inspection of the tubes, after a trial period, will indicate whether the temperature need be raised to get complete solution within the desired time. As noted previously, perchloric acid probably is not satisfactory as the oxidizing agent if the reaction is to be conducted below 250° C, or if there is organic matter present in the sample.

4. DIMENSIONS OF REACTION TUBE

The tube should be no larger than is necessary to accommodate, when half to two-thirds full, the quantity of acid to be used. For the amounts of acid needed for 1 to 1.5 g samples, heavy-walled Pyrex tubes of 15 mm bore, about 20 cm long, with 4- by 8-mm stems (see fig. 1) are very satisfactory. If larger samples are to be treated it will be desirable to increase the length of the tubes, rather than their diameter, or to divide the sample among several tubes.

5. PROTECTION AND HANDLING OF THE SEALED TUBES

The technique of filling, sealing, protecting and opening such tubes is described elsewhere.[10] The filled and sealed tubes are placed in a steel shell, provided with a cap and gasket, into which previously has been placed sufficient calcium carbonate to neutralize all the acid in the tube in the unexpected event of its breaking. Solid carbon dioxide is then added in an amount calculated to give the desired pressure at the operating temperature. These approximate pressures to be expected

[10] C. L. Gordon, W. G. Schlecht, and E. Wichers, *Use of sealed tubes for the preparation of acid solutions of samples for analysis or for small scale refining: Pressures of acids heated above 100° C*, J. Research NBS 33, (1944) RP1622.

by heating acid mixtures can be predicted as being nearly that of the hydrochloric acid used, provided the ratio of hydrochloric acid to oxidant is at least 10:1. Hence the use of hydrochloric acid of 23, 37, and 48 weight-percent HCl in the amount of slightly less than one-half ml in 1 ml of internal capacity of the sealed tube may be expected at 300° C to reach pressures of at least 2,000, 3,630, and 4,730 lb/in.^{2}, respectively. The amounts of solid carbon dioxide that produce these pressures at 300° C are 0.14, 0.24, and, 0.31 g of CO_2 per ml of free space surrounding the sealed tube.

After the carbon dioxide has been introduced the cap is quickly screwed on and the shell is immersed in water to test for leakage of the carbon dioxide around the gasket. The shell is then tilted gently a few times to distribute the sample within the tube, then placed horizontally in an oven and heated to the desired temperature. After cooling and removing the tube from the shell, it is chilled by immersion in a slush of dry ice in a 1:1 mixture of chloroform with carbon tetrachloride. This lowers the internal pressure sufficiently so that the tube can be opened without danger.

If osmium or ruthenium is thought to be present, immerse the opened end of the tube in a solution of approximately 20 weight-percent of HCl saturated with sulfur dioxide, and allow the contents of the tube to drain into this solution, so that the volatile oxides of ruthenium and osmium will not escape. If this is done, the solution should be evaporated and digested with hydrochloric acid to decompose sulfite complexes of the platinum metals before proceeding with the analysis.

WASHINGTON, May 25, 1944.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1615

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IMPROVED REFLUX REGULATOR AND HEAD FOR LABORATORY DISTILLING COLUMNS[1]

By Charles B. Willingham[2], and Frederick D. Rossini

ABSTRACT

A reflux regulator and head for laboratory distilling columns is described that is an improvement over the one previously in use (see J. Research N. B. S. 23, 509 (1939) RP1249) in the distillation laboratory at the National Bureau of Standards in connection with the work of the American Petroleum Institute Research Project 6. The improvements are in better measurement of the temperature of the liquid-vapor equilibrium, in reduction of the hold-up, and in increase in the mechanical strength.

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I. INTRODUCTION

A reflux regulator and head for laboratory distilling columns that was used through 1943 in the distillation laboratory at the National Bureau of Standards in connection with the work of the American Petroleum Institute Research Project 6 was previously described [1].[3] Because of the then limited height (135 inches) in the distillation laboratory, the previously described head was so designed as to require a minimum of space (about 6 inches) between the ceiling and the top of the packing in the rectifying section of the distilling column. This requirement was met by means of certain compromises in design that were no longer necessary when the laboratory was moved at the end of 1943 to a new location having a ceiling height of about 320 inches. This paper describes the improved reflux regulator and head for laboratory distilling columns for use in locations having adequate height. The improvements are in better measurement of the temperature of the liquid-vapor equilibrium, in reduction of the hold-up, and in increase in mechanical strength.

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[3] The figures in brackets indicate the literature references at the end of this paper.

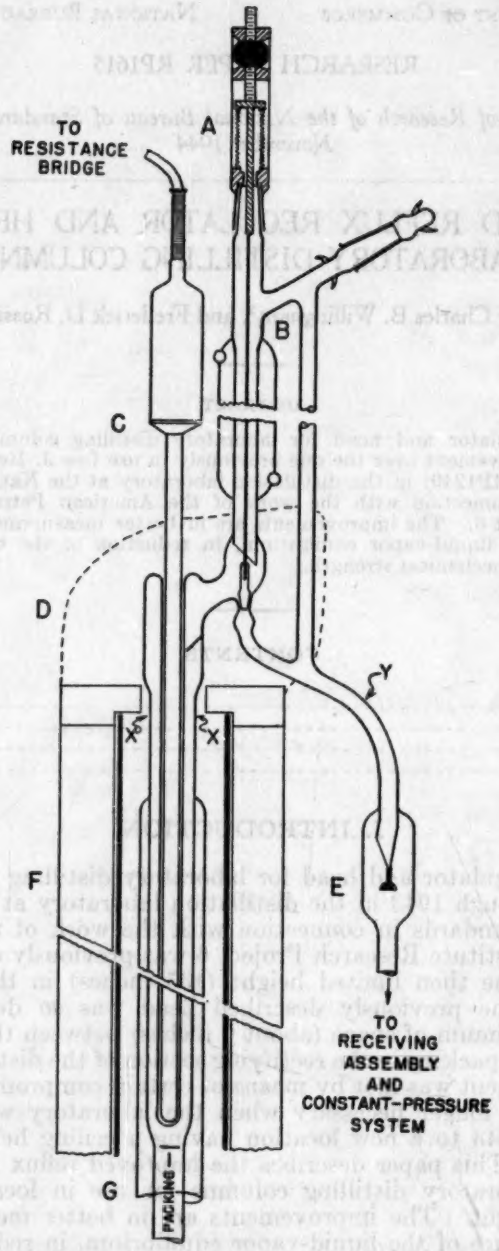

FIGURE 1.—*Assembly of reflux regulator and head.*

A, Metal housing and control, with metallic bellows, as described in figure 3 of reference [1]; *B*, Pyrex-glass part of the apparatus, as shown in figure 2 of this paper; *C*, platinum-resistance thermometer (a thermoelement or other thermometer may be used); *D*, boundary of the thermal insulation on the finished head; *E*, drop counter, with dimensions as shown in figure 2 of reference [1]; *F*, top of jacket assembly; *G*, top of rectifying section, showing vacuum jacket; *X*, *Y*, places where the glass head (as shown in figure 2 of this paper) is sealed to the rectifying section and to the drop counter, respectively.

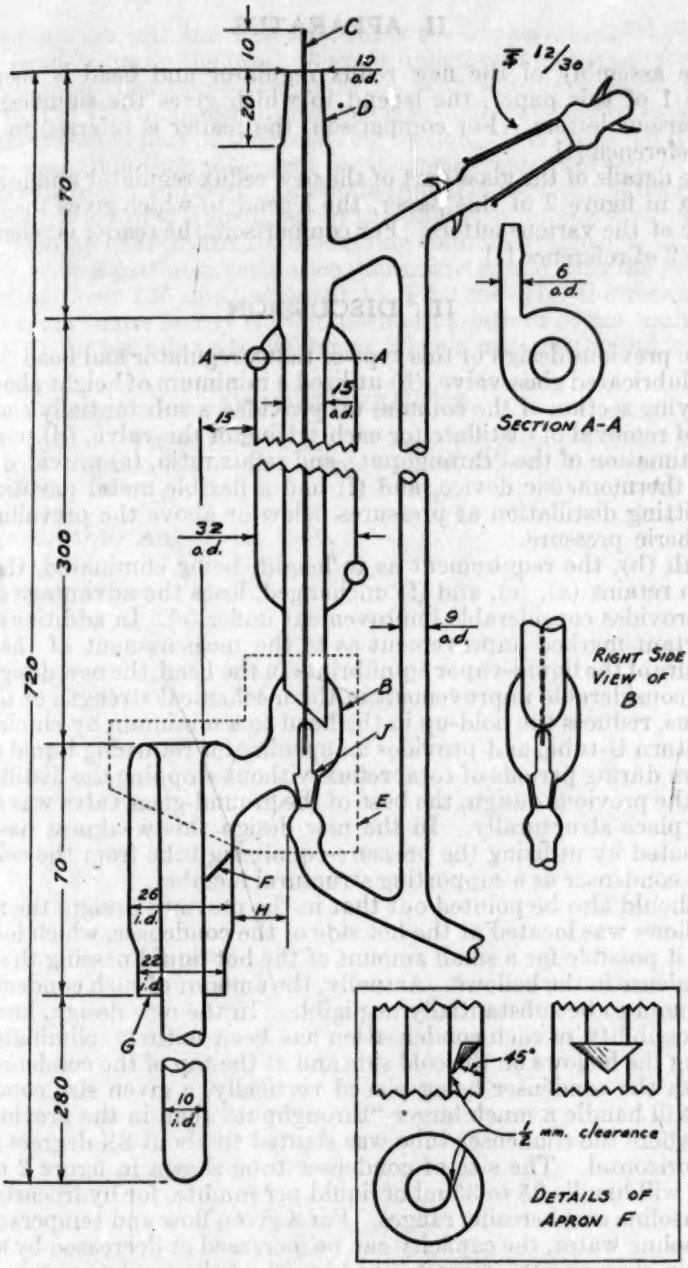

FIGURE 2.—*Details of the glass part of the apparatus.*

A, Section showing opening in jacket of condenser; *B*, portion connecting condenser with ground-glass valve; *C*, tungsten rod, No. 12 AWG; *D*, male ground joint, standard taper, 12/20; *E*, portion having extra-heavy wall; *F*, apron to direct liquid from the condenser to the thermometer well; *G*, bottom edge for sealing to rectifying tube (should be smooth and have its plane perpendicular to the axis of the thermometer well); *H*, clearance (to be not less than 15 mm); *J*, ground-glass valve, taper 1 in 5, small end 4 mm, large end 6 mm, length 10 mm, ground for high vacuum. Pyrex laboratory glass; entire assembly to be thoroughly annealed. Note: All dimensions in millimeters.

II. APPARATUS

The assembly of the new reflux regulator and head is shown in figure 1 of this paper, the legend to which gives the significance of the various letters. For comparison, the reader is referred to figure 1 of reference [1].

The details of the glass part of the new reflux regulator and head are shown in figure 2 of this paper, the legend to which gives the significance of the various letters. For comparison, the reader is referred to figure 2 of reference [1].

III. DISCUSSION

The previous design of this type of reflux regulator and head (a) had a nonlubricated glass valve, (b) utilized a minimum of height above the rectifying section of the column, (c) provided a substantially constant rate of removal of distillate for each setting of the valve, (d) provided for estimation of the "throughput" and reflux ratio, (e) provided space for a thermometric device, and (f) had a flexible metal partition for permitting distillation at pressures below or above the prevailing atmospheric pressure.

With (b), the requirement as to height, being eliminated, the new design retains (a), (c), and (f) unchanged, loses the advantage of (d), and provides considerable improvement under (e). In addition to the important marked improvement as to the measurement of the temperature of the liquid-vapor equilibrium in the head, the new design provides considerable improvement in the mechanical strength of the apparatus, reduces the hold-up in the head to a minimum by eliminating the return U-tube, and provides an opening for returning liquid to the column during periods of total reflux without stopping the distillation.

In the previous design, the base of the ground-glass valve was a very weak place structurally. In the new design this weakness has been eliminated by utilizing the pressure-equalizing tube from the cold end of the condenser as a supporting structural member.

It should also be pointed out that in the previous design, the metallic bellows was located at the hot side of the condenser, which location made it possible for a small amount of the hot liquid passing the valve to condense in the bellows. Actually, the amount of such condensation was found to be substantially negligible. In the new design, however, the possibility of such condensation has been entirely eliminated by placing the bellows on the cold side and at the top of the condenser.

With the condenser being placed vertically, a given size condenser tube will handle a much larger "throughput" than in the previous design, where the condenser tube was slanted to about 8½ degrees above the horizontal. The size of condenser tube shown in figure 2 of this paper will handle 25 to 35 ml of liquid per minute, for hydrocarbons of the gasoline and kerosine ranges. For a given flow and temperature of the cooling water, the capacity can be increased or decreased by appropriately changing the diameter and length of the condenser tube. For use in this laboratory, a larger size, to handle 40 to 60 ml of liquid per minute, has been made with changes in the dimensions of the condenser, as follows: Length of condenser tube, increase from 300 to 360 mm; diameter of inner and outer tubes of condenser, increase from 15 to 18 mm and from 32 to 35 mm, respectively.

In connection with the measurement of the temperature of the liquid-vapor equilibrium in the head, the new design provides space for a 25-ohm platinum resistance thermometer, with adequate depth of immersion, the thermometer proper being actually well down inside the vacuum-jacketed part of the rectifying section. If it is desired to use a multiple junction thermoelement for the measurement of temperature, both the diameter and length of the thermometer well can be decreased.

An indication of the adequacy of the provision for the thermometer is provided by the fact that in a distilling column arranged as shown in figure 1, with a platinum resistance thermometer and with the pressure controlled (near 725 mm) constant to ± 0.2 mm Hg, the readings of temperature taken hourly showed normal variations of not more than $\pm 0.01°$ C, for periods up to 200 hours, when a pure compound was distilled [2].

IV. REFERENCES

[1] F. D. Rossini and A. R. Glasgow, Jr., J. Research NBS **23**, 509 (1939) RP1249.
[2] C. B. Willingham and F. D. Rossini, National Bureau of Standards. Unpublished data.

WASHINGTON, August 15, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPERR P1616

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PREPARATION OF SALTS OF GALACTURONIC ACID FROM BEET PULP

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

This investigation demonstrates that dried beet pulp can be hydrolyzed by a commercial pectic enzyme, and that calcium galacturonate, sodium calcium galacturonate, and sodium strontium galacturonate can be obtained readily from the hydrolyzate. The crystalline salts are obtained by neutralization of the hydrolyzate with suitable bases, followed by concentration. Samples of dried beet pulp gave calcium galacturonate, sodium calcium galacturonate, and sodium strontium galacturonate in yields corresponding to 105 g, 227 g, and 255 g/kg, respectively.

It is also shown that sodium strontium galacturonate can be separated, at least in some cases, directly from silage drainage liquor. The occurrence of galacturonic acid in the drainage liquor suggests the possibility of developing a process in which hydrolysis is effected by organisms grown in beet pulp.

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I. INTRODUCTION

In connection with the development of a process for the synthesis of vitamin C [1],[1] a cheap source of galacturonic acid was needed. In 1932 Ehrlich found that the polygalacturonide, now known as pectic acid, a product of the hydrolysis of the original pectic substances of plants, when treated with an enzyme prepared from a "*Penicillium ehrlichii*," gives galacturonic acid in high yield [2]. Even prior to that time, Willaman and Kertesz had developed a method and enzyme for effecting the hydrolysis of pectic substances in fruit juices [3]. Shortly thereafter a pectic enzyme preparation, presumably the same as that of Willaman and Kertesz, was produced by Rohm and Haas and sold under the trade name of "Pectinol." A process developed by Mottern and Cole [4] involved treating pectic acid with Pectinol and extracting galacturonic acid from the hydrolyzate with ethyl alcohol. Pigman [5] improved the process by the use of methyl alcohol instead of ethyl alcohol. Although the method is fairly simple, it is nevertheless expensive because of the cost of the pectic acid and of the alcohol required in separating the galacturonic acid from the accompanying impurities. A study was therefore made of the salts of galacturonic acid with the object of finding a salt of relatively low solubility, which would be suitable for the separation of the acid [6]. In the course of the work 12 new crystalline salts were prepared. Several of these, especially sodium strontium galacturonate, sodium calcium galacturonate,[2] and calcium galacturonate were found to be useful for the separation of galacturonic acid from solutions containing substantial amounts of impurities. The way was thus opened for the preparation of galacturonic acid from the hydrolyzates of plant materials by separating the acid as a difficultly soluble salt. It has been known for some time that the pulp remaining after the separation of sugar from sugar beets, contains substantial quantities of pectic substances, which can be hydrolyzed to yield arabinose, galactose, methyl alcohol, acetic acid, and galacturonic acid [7]. Hence beet pulp provides a vast potential source of galacturonic acid. The application of the new salts to the separation of galacturonic acid from hydrolyzates of beet pulp is the subject of the present paper. In a separate publication [8] the use of sodium strontium galacturonate for the preparation of galacturonic acid from citrus pectic acid, pectin, and the residues of the citrus fruit industry is reported.

II. ENZYMATIC HYDROLYSIS OF DRIED BEET PULP

There are at least three types of enzymes involved in the hydrolysis of pectic substances: protopectinase, pectase, and pectinase [9]. Protopectinase causes the formation of soluble pectins from protopectin, the original pectic substance; pectase removes the methoxyl groups from soluble pectins, leaving pectic acid, which in the presence of calcium or other alkaline earth salts forms gels; pectinase causes hydrolysis of the glycosidic linkages in pectins and pectic acid, with the formation of galacturonic acid, arabinose, galactose, and other simple substances. Ehrlich discovered a mold growing on sugar beets, *Penicillium ehrlichii*, and used it for the preparation of an enzyme which causes complete hydrolysis of

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] This salt was prepared independently by R. Pasternack and P. P. Regna. See U. S. Patent 2,338,534 (1944).

pectic acid [2]. He also obtained an active protopectinase preparation from *Penicillium glaucum*, and showed that in small quantity it causes extensive dissolution of beet pulp [10]; he did not report the composition of the resulting hydrolyzate.

The availability of a commercial pectic enzyme, and of the difficultly soluble salts of galacturonic acid, led to our attempt to prepare galacturonic acid directly from beet pulp. It was known that Pectinol causes complete hydrolysis of pectic acid [4] and of soluble pectins [11], but it was not known whether it would attack the protopectin in the cell walls of the beet root.

When dried beet pulp [3] in water suspension was treated with Pectinol, a large portion of the pulp liquefied within the first 2 days, and the mixture became strongly acid. In our early experiments, the acidity was adjusted at the beginning to pH 3.7, approximately the optimum point for the hydrolysis of pectic acid by the enzyme. It was found, however, that the acidity of the beet pulp-Pectinol mixture soon approached the optimum point without the addition of acid, and hence the preliminary acid treatment was discontinued. The increase in acidity may be ascribed to the presence of an esterase in the enzyme preparation. The conversion of over 65 percent of the dried pulp to soluble solids shows that Pectinol contains an enzyme (protopectinase) that attacks the original pectic substances of the beet root. The amount of hydrolysis depends to some extent upon the amount of the enzyme used, but there is no direct proportion. Thus 46 percent of the pulp was converted to soluble solids in 2 weeks by the action of 5 g of Pectinol per kilogram of beet pulp, whereas 66 percent of the pulp was converted by the action of 100 g of Pectinol. Because of the heterogeneous character of the beet pulp-Pectinol mixture, calculation of the velocity constants was not attempted. A few curves, however, are given in figure 1 to show some of the changes that take place during the hydrolysis. In other experiments the hydrolyzate was analyzed, and the galacturonic acid was separated in the form of the calcium, sodium calcium, or sodium strontium salt. These substances were prepared under strictly comparable conditions in order to ascertain their relative merits for the separation of galacturonic acid. The results show that sodium strontium galacturonate crystallizes from hydrolyzates of beet pulp in the highest yield, but all three salts have value for the separation of galacturonic acid from the hydrolyzates of pectic substances. Sodium strontium galacturonate was obtained in the amount of 250 g/kilogram of dried beet pulp.

In addition to galacturonic acid, the beet pulp hydrolyzate contained substantial quantities of acetic acid and L-arabinose. In a commercial process the acetic acid might be reclaimed by distillation and the L-arabinose might be separated from the mother liquor obtained after crystallization of the galacturonate. The feasibility of separating L-arabinose was shown by the preparation of the crystalline sugar from the liquor in yield corresponding to 62 g/kg of dried pulp (see p. 397). It is of interest to note in this connection that L-arabinose was originally prepared from beet pulp, and that this

[3] Dried beet pulp was studied because the work was conducted at some distance from the source of supply, and at periods when the fresh pulp was not available. On account of the high temperatures employed in the drying process, some changes may have taken place in the pectic substances originally in the pulp. For this reason, the behavior of dried pulp may not be strictly comparable to that of fresh pulp. In a commercial process, fresh pulp could be employed, with a preliminary heat treatment to facilitate dissolution, and destroy objectionable micro-organisms.

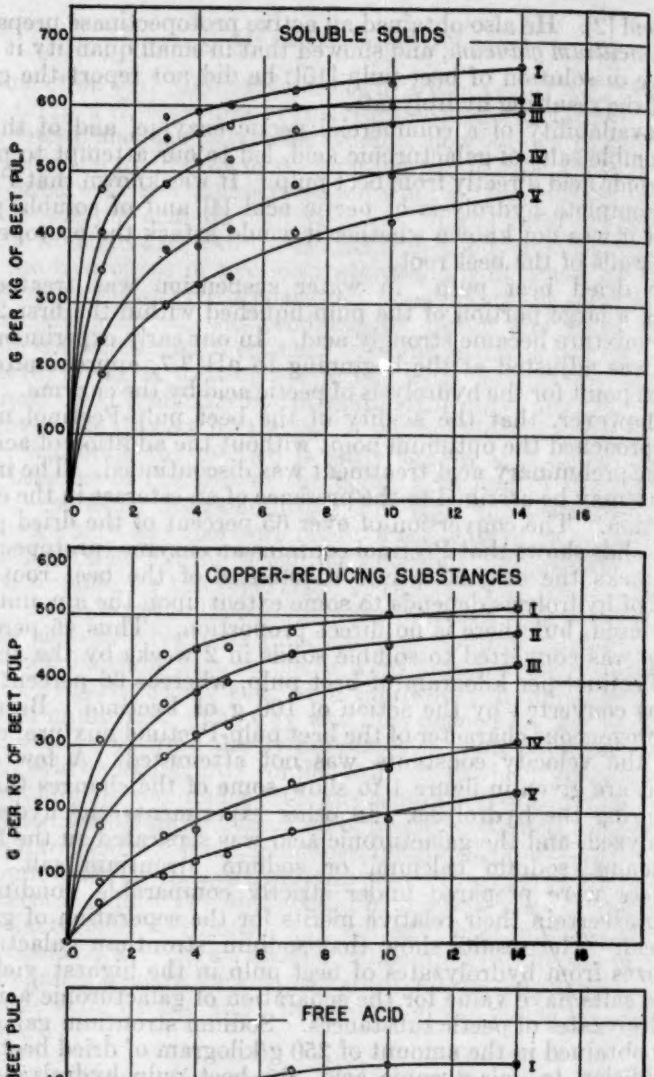

FIGURE 1.—*Analytical data for hydrolyzates from beet pulp treated with various quantities of a pectic enzyme.*

I. 5.0 g of Pectinol plus 50 g of pulp plus 500 ml of water at 35° C. II. 2.5 g of Pectinol plus 50 g of pulp plus 500 ml of water at 35° C. III. 1.5 g of Pectinol plus 50 g of pulp plus 500 ml of water at 35° C. IV. 0.5 g of Pectinol plus 50 g of pulp plus 500 ml of water at 35°C. V. 0.25 g of Pectinol plus 50 g of pulp plus 500 ml of water at 35° C.

material is still considered to be one of the best sources of arabinose [12].

III. ENZYMATIC HYDROLYSIS OF BEET PULP DURING THE SILOING PROCESS

During the storage of beet pulp in silos, there sometimes occurs considerable liquefaction of the pulp; this condition has been observed frequently in certain districts, in others rarely. It seemed possible that the liquefaction of the pulp in the silos might have been caused by enzymes generated by micro-organisms similar to the mold isolated by Ehrlich, and that silage drainage liquor might provide a source of galacturonic acid. An analysis of a sample of silage drainage liquor, p. 399, showed the presence of substantial quantities of galacturonic acid and arabinose. However, the low copper-reduction value of the silage drainage liquor indicates that a considerable part of the galacturonic acid and arabinose was not in the free state, and hence it appears that hydrolysis of the original pectic substance was only partially complete. Presumably the liquor contained soluble pectins and pentosans, together with free galacturonic acid. Neutralization of the liquor with a mixture of sodium bicarbonate and strontium carbonate in equimolecular proportions gave a solution which, on concentration, yielded crystalline sodium strontium galacturonate. The occurrence of galacturonic acid in the silage drainage liquor is noteworthy because the organisms in the silo might have utilized the galacturonic acid to form lower acids and other degradation products. Undoubtedly, under more favorable conditions, the hydrolysis in the silo could be effected more completely and with larger yields of galacturonic acid.

IV. POSSIBLE SOURCES OF PECTIC ENZYMES

These studies suggest the possibility of developing a method for obtaining galacturonic acid from pectic substances by inoculating fresh beet pulp with organisms known to yield protopectinase and pectinase. The enzyme could be brought in contact with the pulp by percolation of water through the mold growth which forms on top of the silo. However, a batch process, such as that used in the malting of grain, might prove more practicable.

Since pectic enzymes are produced in the growth of numerous molds, and occur in the culture media, it seems possible that the enzymes could be obtained economically as byproducts of certain industries. Possible sources are the aqueous solution remaining after the separation of penicillin, or the culture media of molds grown for food purposes.

V. USE OF PECTIC ENZYMES FOR ANALYTICAL PURPOSES

The material made soluble by treatment of plant products with pectic enzymes constitutes an important group of carbohydrates markedly different from crude fiber, sugar, or starch. The extensive liquefaction of beet pulp observed in this investigation suggests the use of enzymatic degradation in the analysis of feeds and food products. For convenience, material made soluble by a definite treatment with a pectic enzyme preparation could be designated as "pectic enzyme-soluble

substances." Thus an analysis of dried beet pulp might include moisture, fat, protein, crude fiber, ash, and pectic enzyme-soluble substances. The determination of the pectic enzyme-soluble fraction is suggested in place of the fraction ordinarily designated "nitrogen-free extract," since the latter is open to serious objection. (See p. 10 of [13].) The determination of the pectic-enzyme soluble fractions of representative samples of the more common vegetables and fruits would constitute a worthwhile project.

VI. EXPERIMENTAL DETAILS

1. MATERIALS

The dried beet pulp used was kindly supplied by the Great Western Sugar Co. Most of the work was conducted on a sample of dried pulp from Bayard, Nebr., the label of which carried the following data:

Crude protein, not less than	7.0%
Crude fat, not less than	0.3%
Crude fiber, not more than	22.5%
Nitrogen-free extract, not less than (composed only of residue of sugar beets dried after extraction of sugar).	48.0%

Before use, the pulp was extracted with water in a conical percolator until the wash water gave no test for sugar. The pulp was then air-dried for a period of several weeks, after which time it gave the following analytical data:

Moisture	8.21%
Ash	2.77%
Galacturonic acid, (CO_2 method)	26.0%
Arabinose	22.2%

The silage drainage, likewise supplied by the Great Western Sugar Co., was obtained from a silo showing excessive loss due to liquefaction. The sample was taken at Loveland, Colo., in February 1943. It was protected from mold growth by the addition of toluene and stored in a refrigerator until analyzed.

The enzyme used here, Pectinol-46AP, was purchased from Rohm and Haas, Philadelphia, Pa. It had been standardized by the manufacturer to an activity arbitrarily designated 100D.

2. ANALYTICAL METHODS

(a) SOLIDS

The total solids in the hydrolyzate were determined by drying a 5-ml sample on pure quartz sand to constant weight in a vacuum oven at 60° C and a pressure of approximately 5 mm. A higher temperature was not used because of the instability of galacturonic acid.

(b) VOLATILE ACIDS

Volatile acids were determined by steam distillation, and titration of the distillate with standard alkali, as described on p. 167 of [14].

(c) COPPER-REDUCING SUBSTANCES

The copper-reduction values were determined on neutralized samples of the hydrolyzate by a modified Scales method [15]. Be

cause of the slowness with which galacturonic acid reacts, it was necessary to increase the boiling time to 10 minutes. Factors were determined for a mixture of galacturonic acid and arabinose in the proportion in which they were found in the hydrolyzate. Presumably the solutions contained galactose in addition to galacturonic acid and arabinose; the galactose factor, however, does not differ widely from the factor (1.25 mg/ml of 0.04 *N* iodine) determined for the mixtures. Hence, the value 1.25 was used in estimating the quantity of reducing substances.

(d) GALACTURONIC ACID

The substance was determined by the method of Lefèvre and Tollens [16], essentially as described by Ehrlich, p. 1661 of [7].

(e) FURFURAL

The determination was made by the procedure described on p. 362 of [14].

(f) ARABINOSE

The amount of arabinose in the hydrolyzate was calculated by the method of Ehrlich and Schubert [17]. Both galacturonic acid and arabinose yield furfural when heated with 12-percent hydrochloric acid. By subtracting the amount of furfural phloroglucide equivalent to the galacturonic acid (weight of galacturonic acid divided by 2.64) from the weight of phloroglucide found, the amount of phloroglucide produced from the arabinose was ascertained; by use of Kröber's table (p. 686 of [14]) the corresponding weight of arabinose was found. To establish the identity of the pentose responsible for the production of furfural, crystalline L-arabinose was separated from the hydrolyzates as described on p. 397.

(g) GALACTOSE

The difference between the copper-reducing substances and the sum of galacturonic acid and arabinose was taken to be galactose, a substance which Ehrlich and Sommerfeld reported to be a constituent of the pectic acid prepared from beet pulp [18].

3. INVESTIGATION OF DRIED BEET PULP

(a) EFFECT OF CONCENTRATION OF ENZYME

In order to ascertain the quantity of enzyme required to effect satisfactory hydrolysis of dried beet pulp, samples of the pulp were treated with various quantities of Pectinol, and the amount of hydrolysis was followed by the determination of soluble solids, reducing sugar, and free acid. Each hydrolysis mixture was prepared by the addition of Pectinol to 50 g of beet pulp in 500 ml of water contained in a 1-liter glass-stoppered Erlenmeyer flask. Mold growth was inhibited by the addition of 10 ml of toluene, and the flasks were maintained at a temperature of 35° C for 2 weeks. From time to time representative samples of the reaction mixtures were withdrawn and soluble solids, copper-reducing substances, and free acid were determined on the filtered hydrolyzates. The results are shown in figure 1. The curves reveal that even with large quantities of the enzyme, hydrolytic reactions take place over a period of at least 2 weeks and that the extent of hydrolysis increases with increasing

amounts of enzyme. Because of the heterogeneous nature of the be pulp-enzyme mixture and the complex character of the reactions, quantitative interpretation of the data has not been include Measurements were not made with mixtures containing more than part of enzyme to 10 parts of beet pulp.

(b) PROPERTIES AND COMPOSITION OF THE HYDROLYZATE

To study the properties and composition of the hydrolyzate mo closely, a mixture of 1 kg of dried beet pulp, 100 g of Pectinol, 10 lite of water, and 100 ml of toluene was allowed to stand at 35° C, wi occasional stirring. After 10 days, the mixture was filtered through Büchner funnel and the material on the funnel was washed with h water and dried. It weighed 378 g, which, after allowance for t insoluble portion of the Pectinol (63 g), gave a weight of 315 g for t insoluble residue of the beet pulp. The filtrate and washings we combined and used for analysis (table 1). The sum of moisture in t original pulp (82 g), insoluble residue of the hydrolyzate (315 g), a soluble solids in the hydrolyzate (560 g) is only 957 g. The differen from the weight of the original pulp is 43 g, presumably volati substances such as acetic acid and methyl alcohol. The volatile ac actually determined was 0.60 equivalent, or, expressed as acetic ac 36 g.

TABLE 1.—*Analysis of the filtered hydrolyzate* [a]

Optical rotation, °S in a 2-dm tube	*23. 6
Refractive index, N_D^{20}	*1. 3427
Acidity, pH	*3. 4
Soluble solids	560 g
Ash	32. 2 g
Ca	4. 86 g
Mg	3. 15 g
Volatile acid	0. 60 equivalent
Free acid	1. 05 equivalent
Copper-reducing substances (modified Scales method)	488 g
Galacturonic acid (CO_2 method)	236 g
Arabinose [b] (furfural method)	214 g
Galactose (by difference)	38 g

[a] All values, except those marked with the asterisk, are based on the total hydrolyzate from 1 kg of a dried beet pulp containing 8.2 percent of moisture. The volume of the hydrolyzate and wash liquor w 21.7 liters.

[b] A sample of the hydrolyzate corresponding to 1 g of beet pulp gave 0.2783 g of furfural phloroglucide the method of p. 362 of [14]. Presumably, 0.0894 g of the phloroglucide was derived from the galacturo acid. The remainder, 0.1889 g corresponds to 0.214 g of arabinose or to 0.172 g of pentosans.

(c) SEPARATION OF CARBOHYDRATE CONSTITUENTS FROM THE HYDROLYZAT

One kilogram of dried beet pulp was treated with 100 g of Pectin in 10 liters of water in the manner previously described. The analy ses of the filtered hydrolyzate showed the presence of 220 g of ga acturonic acid and of 1.16 equivalents of free acid. The liquor wa divided into portions, from which were prepared sodium calciu galacturonate, sodium strontium galacturonate, and calcium gala turonate, respectively. The mother liquor from the preparation sodium strontium galacturonate was used for the preparation arabinose.

(1) *Sodium calcium galacturonate.*—One-third of the hydrolyzate described above was digested with 12.8 g of calcium carbonate at 70° C. When reaction was complete, 10.8 g of sodium bicarbonate was added, and the solution was filtered and evaporated under reduced pressure to a volume of 500 ml. The solution was seeded with crystalline sodium calcium galacturonate and allowed to stand in a refrigerator until crystallization was complete. The resulting crystals were collected on a filter, washed with a little cold water, and dried. The product weighed 68.5 g and was substantially pure sodium calcium galacturonate. The mother liquor was saturated with ethyl alcohol, and after 1 day, the resulting crystals (7.0 g) were separated. The yield of sodium calcium galacturonate in the first crop was 20.6 percent of the weight of the dry beet pulp, or 72.5 percent of the salt theoretically obtainable from the galacturonic acid in the hydrolyzate. The total yield (75.5 g) which was 22.7 percent of the weight of the pulp, corresponds to 79.9 percent of the galacturonate acid in the hydrolyzate.

(2) *Sodium strontium galacturonate.*—This substance was prepared from one-third of the hydrolyzate in the same manner as sodium calcium galacturonate, except that 18.8 g of strontium carbonate was used in place of the calcium carbonate. The crop of crystals obtained directly from the aqueous solution weighed 77.7 g; a second crop obtained from the mother liquor by the addition of 50 ml of 95-percent ethyl alcohol weighed 7.2 g. The yield from aqueous solution was 23.3 percent of the dry pulp, corresponding to 77.3 percent of the galacturonic acid in the hydrolyzate. The total yield of sodium strontium galacturonate (84.9 g) was 25.5 percent of the pulp, corresponding to 84.5 percent of the galacturonic acid in the hydrolyzate. The mother liquor that remained after crystallization of the salt was used for the preparation of L-arabinose.

(3) *Calcium galacturonate.*—The remaining third of the hydrolyzate was digested at 70° C with 19.1 g of calcium carbonate until reaction was complete, and the solution was concentrated under reduced pressure to a volume of 500 ml. It was seeded with crystalline calcium galacturonate and allowed to stand in a refrigerator until crystallization was complete. The crystals of calcium galacturonate, when separated and air-dried, weighed 25 g. A second crop of 10 g was obtained by saturation of the mother liquor with ethyl alcohol. The yield of calcium galacturonate in the first crop was 7.5 percent of the weight of the dry beet pulp and corresponds to 29.8 percent of the salt theoretically obtainable from the galacturonic acid in the hydrolyzate. The total yield of the salt was 10.5 percent of the weight of the pulp, and corresponds to 41.7 percent of the galacturonic acid in the hydrolyzate.

(4) L-*Arabinose.*—Although beet pulp has been used for the preparation of arabinose [12], higher yields are obtained from cherry gum [19] or from mesquite gum [20]. The process described here for the preparation of galacturonic acid from beet pulp hydrolyzates yields sirupy residues suitable for the preparation of arabinose. The arabinose may be separated by essentially the same method as that previously used for the separation of arabinose from the hydrolyzates of cherry gum or of mesquite gum.

The mother liquor from the preparation of sodium strontium galacturonate was evaporated under reduced pressure to a thick sirup. This was extracted with three 500-ml portions of hot 95-percent ethyl alcohol. The combined extracts were cooled to room temperature and filtered after the addition of 25 g of a decolorizing carbon. The alcoholic solution was evaporated to 150 ml, diluted with 50 ml of glacial acetic acid, and seeded with crystalline L-arabinose. After 3 days, the crystals, which formed, were collected on a filter, washed with 30 ml of acetic acid in four portions, and dried. The crystalline arabinose so obtained weighed 22.0 g and gave an equilibrium specific rotation of +98.4°. Since pure L-arabinose has an equilibrium specific rotation of +104°, the purity of the crude product is 94.6 percent, and the yield of pure arabinose corresponds to 62.4 g/kg of dried beet pulp, or 29 percent of the amount in the hydrolyzate. The low yield suggests that part of the arabinose was present as arabans.

4. INVESTIGATION OF SILAGE DRAINAGE LIQUOR

From the analysis of the silage drainage liquor reported in table 2, it will be noted that the liquor gave carbon dioxide equivalent to 10.7 g of galacturonic acid per liter and furfural equivalent to 11.5 g of arabinose, or 9.2 g of pentosans. The copper-reducing substances, however, were only 6.1 g per liter. These results indicate that the galacturonic acid is present in part in the form of soluble pectins and the arabinose in the form of arabans. The presence of some free galacturonic acid was shown by the separation of crystalline sodium strontium galacturonate in the following manner:

Eighteen liters of the liquor was digested with 50 g of strontium carbonate at 70° C. When reaction was complete, 30 g of sodium bicarbonate was added. The mixture was filtered with the aid of a decolorizing carbon, and the filtrate was concentrated in a vacuum still to a volume of 1 liter. The solution was seeded with crystalline sodium strontium galacturonate and allowed to stand in the refrigerator for several days. The crystals, which separated, were collected on a filter, washed with a small quantity of water, and finally dried. The product weighed 31 g, and a second crop of 6.8 g was obtained by the addition of alcohol to the mother liquor. The crude salt was recrystallized twice from hot water and identified as sodium strontium galacturonate by its optical rotation and by a mixed solubility determination with authentic sodium strontium galacturonate. The yield of sodium strontium galacturonate from the silage drainage corresponds to 14.3 percent of the galacturonic acid found by analysis. Although the yield is low, the separation of the crystalline salt from the silage drainage, without involved purification steps, demonstrates the possibility of obtaining galacturonic acid from beet pulp through the action of enzymes produced by organisms grown on the pulp.

TABLE 2.—*Analysis of silage drainage liquor*

Refractive index, N_D^{20}	1.3380.
Acidity, pH	3.5.
Soluble solids	31.2 g/liter.
Ash	1.9 g/liter.
Volatile acid	0.153 equivalent per liter.
Free acid	0.173 equivalent per liter.
Copper-reducing substances	6.1 g/liter.
Galacturonic acid	10.7 g/liter.
Pentosans *	9.2 g/liter.

* A 10-milliliter sample of the silage drainage gave 0.1391 g of furfural phloroglucide, of which 0.0405 g was presumably derived from the galacturonic acid. The remainder corresponds to 0.115 g of arabinose or to 0.092 g of pentosans.

VII. SUMMARY

Treatment of certain samples of dried beet pulp with a commercial pectic enzyme caused hydrolysis of the original pectic substances, and the dissolution of about 65 percent of the dry substance. The hydrolyzate from 1 kg of dried pulp contained appoximately 236 g of galacturonic acid, 214 g of arabinose, 38 g of galactose, and 36 g of acetic acid. The galacturonic acid in the hydrolyzate was separated as calcium galacturonate in 42-percent yield, as sodium calcium galacturonate in 80-percent yield, and as sodium strontium galacturonate in 85-percent yield. The mother liquor from the preparation of sodium strontium galacturonate gave L-arabinose in 29-percent yield. Because of exceptionally good crystallizing properties, sodium strontium galacturonate appears to be the most suitable salt for the separation of galacturonic acid from the hydrolyzates of plant materials.

It was found that the drainage liquor from a beet pulp silo in which there had been excessive liquefaction contained approximately 10 g of galacturonic acid per liter and that part of this material could be reclaimed in the form of sodium strontium galacturonate without the use of a commercial enzyme. The separation of a salt of galacturonic acid from the drainage liquor suggests the possibility of developing a process in which hydrolysis is effected by organisms grown in the moist beet pulp. It is also suggested that the aqueous solutions which remain after the separation of penicillin, or the culture media of molds grown for food purposes may ultimately provide a source of pectic enzymes for use in the preparation of galacturonic acid from beet pulp or other pectic substances.

The authors express their appreciation to S. J. Osborn, of the Great Western Sugar Co., for his cooperation in providing the samples of beet pulp and silage drainage liquor used in the investigation, and to Nancy Holt, of this Bureau, for her assistance in the analytical work.

VIII. REFERENCES

[1] H. S. Isbell, J. Research NBS **33,** 45 (1944) RP1594.
[2] F. Ehrlich, Biochem. Z. **251,** 204 (1932).
[3] J. J. Willaman and Z. I. Kertesz, New York State Agr. Expt. Sta. Tech. Bul. 178 (1931); Willaman and Kertesz, U. S. Patent 1,932,833 (1931).
[4] H. H. Mottern and H. L. Cole, J. Am. Chem. Soc. **61,** 2701 (1939).
[5] W. W. Pigman, J. Research NBS **25,** 301 (1940) RP1325.
[6] H. S. Isbell and H. L. Frush, J. Research NBS **32,** 77 (1944) RP1576.
[7] F. Ehrlich, Abderhalden's Handbuch der biologischen Arbeitsmethoden, Abt. 1, Teil 11, 1501–1688 (1936).
[8] H. S. Isbell and H. L. Frush, J. Research NBS **33,** 401 (1944) RP1617.
[9] Z. I. Kertesz, Ergeb. Enzymforsch. **5,** 233 (1936).
[10] F. Ehrlich, Biochem. Z. **250,** 525 (1932).
[11] E. Rietz and W. D. Maclay, J. Am. Chem. Soc. **65,** 1242 (1943).
[12] T. S. Harding, Sugar **24,** 656 (1922).
[13] A. L. Winton and K. B. Winton, The Structure and Composition of Foods, **I,** 10 (John Wiley & Sons, Inc., New York, N. Y., 1932).
[14] Methods of Analysis of the Association of Official Agricultural Chemists (1940).
[15] H. S. Isbell, W. W. Pigman, and H. L. Frush, J. Research NBS **24,** 241 (1940) RP1282.
[16] K. V. Lefèvre and B. Tollens, Ber. deut. chem. Ges. **40,** 4513 (1907).
[17] F. Ehrlich and F. Schubert, Ber. deut. chem. Ges. **62,** 1974 (1929).
[18] F. Ehrlich and R. v. Sommerfeld, Biochem. Z. **168,** 312 (1926).
[19] H. Kiliani, Ber. deut. chem. Ges. **19,** 3029 (1886).
[20] E. Anderson and L. Sands, J. Am. Chem. Soc. **48,** 3172 (1926).

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PREPARATION OF SODIUM STRONTIUM GALACTURONATE FROM CITRUS PRODUCTS

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ABSTRACT

The present paper describes the convenient separation of galacturonic acid in the form of sodium strontium galacturonate from the hydrolyzates of citrus products, namely pectic acid, pectin, and the peel of oranges and of grapefruit. The methods are suitable for the preparation of large or small quantities of the salt, and it is believed that the preparation from pectic acid is commercially practicable. Sodium strontium galacturonate is obtained from pectic acid in about 90-percent yield without the use of alcohol or other organic solvent. By treatment of the salt with an equivalent quantity of aqueous sulfuric acid, a solution is obtained from which about 65 percent of the galacturonic acid may be crystallized in one crop, substantially pure. Additional crops obtained by the use of an organic solvent make the yield nearly quantitative.

Pectin is not quite so satisfactory in the process as pectic acid, but because of its educational value, the preparation of sodium strontium galacturonate from pectin might be included in a course of laboratory instruction to demonstrate the presence of galacturonic acid in pectic substances. Both orange peel and grapefruit peel may be used for the preparation of sodium strontium galacturonate, but the industrial use of these materials does not seem feasible at present on account of the large quantities of relatively expensive enzyme required for hydrolysis.

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I. INTRODUCTION

The possibility of preparing vitamin C from galacturonates [1] [1] makes important the examination of various methods and raw materials for the production of salts of galacturonic acid. In previous papers from this laboratory it has been shown that galacturonic acid can be separated directly from the hydrolyzates of pectic substances in the form of certain new salts, particularly calcium galacturonate, sodium calcium galacturonate and sodium strontium galacturonate [2]. Some of the studies on the preparation of galacturonic acid have been conducted on hydrolyzates of beet pulp [3]. In the course of the work it was found that sodium strontium galacturonate crystal-

[1] Figures in brackets indicate the literature references at the end of this paper.

lizes from crude hydrolyzates in higher yield than the other aforementioned salts. The present paper describes the convenient separation of galacturonic acid in the form of sodium strontium galacturonate from the hydrolyzates of citrus products, namely, pectic acid, pectin and the peel of oranges and of grapefruit. The methods are suitable for the preparation of large or small quantities of the salt, and it is believed that the process described here is commercially practicable.

The use of pectic acid for the preparation of galacturonic acid was studied by Ehrlich [4] and by Link and coworkers [5]. Mottern and Cole [6] improved the process by employing a commercial pectic enzyme for the hydrolysis of pectic acid, and Rietz and Maclay [7] showed that the method was also applicable to the preparation of galacturonic acid from pectin. In the preparation of sodium strontium galacturonate reported here, pectic acid is the most convenient raw material for laboratory use, and the most economical at the present price of the commercial enzyme. Pectin is not quite so satisfactory in the process as pectic acid; however, the preparation of sodium strontium galacturonate from citrus pectin is described, because its educational value and simplicity are such that it might well be included in a course of laboratory instruction to demonstrate the presence of galacturonic acid as a constitutent of pectic substances.

Both orange peel and grapefruit peel may be used for the preparation of crystalline sodium strontium galacturonate. Although a considerable part of the residues from oranges and lemons is used industrially in the preparation of pectin, the residues from grapefruit have at present little use, aside from a small portion, from which naringin, the bitter glycoside of the peel, is extracted [8]. The convenient preparation of sodium strontium galacturonate from grapefruit peel is therefore significant in that it indicates a possible use for this waste product. The hydrolysis of the citrus fruit residues requires a somewhat larger amount of the enzyme than the hydrolysis of purified pectic acid or pectin. Hence the practicability of the direct utilization of the residues depends upon the cost of the enzyme in large quantities, a factor unknown at present. As mentioned in connection with the utilization of beet pulp [3], the culture media from molds grown for the production of penicillin or other substances may ultimately provide an inexpensive source of pectic enzymes.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF SODIUM STRONTIUM GALACTURONATE FROM PECTIC ACID

The pectic acid used in the present investigation was purchased from the California Fruit Growers' Exchange, Ontario, Calif. It contained 98 percent of galacturonic acid as determined by the carbon-dioxide method [9], but analyses of material purchased at various times have differed considerably. The method given here is suitable for a pectic acid having a galacturonic acid content of 95 percent or above. For a pectic acid of lower galacturonic acid content, the amounts of sodium bicarbonate and strontium carbonate should be proportionately adjusted.

A dry mixture consisting of 1,000 g of pectic acid, 150 g of sodium bicarbonate, and 100 g of Pectinol–46AP [2] was added in small por-

[2] The pectic enzyme is manufactured by Rohm and Haas, Philadelphia, who have standardized it by dilution with diatomaceous earth to an activity arbitrarily designated 100D.

ions, with continuous stirring, to 10 liters of water. Excessive foaming was prevented by the addition of a commercial antifoam agent. Sufficient toluene was added to cover the surface of the liquid, and the mixture was allowed to stand at 40° C. After 1 day, 125 g of strontium carbonate was added in portions, and the mixture was seeded with crystals of sodium strontium galacturonate. During the period of hydrolysis the salt crystallized from the hydrolyzate. After a total of 9 days, an additional quantity of 125 g of strontium carbonate was added, and the mixture was allowed to stand in the refrigerator for a day. The salt was then separated by filtration, washed with cold water and dried. The crude product weighed 1,300 g and contained 128 g of water-insoluble material. To crystallize the sodium strontium galacturonate in the filtrate, 25 g of strontium acetate was added and the solution was evaporated under reduced pressure at a temperature below 50° C to a volume of about 500 ml. The concentrated solution was allowed to stand for 1 day in the refrigerator and the crystals which formed (152 g) were separated by filtration. An additional quantity of 54 g was obtained by concentration of the mother liquor. The three crops of crude sodium strontium galacturonate were combined and recrystallized by dissolving the salt in 12 liters of boiling water, filtering the hot solution with the aid of a decolorizing carbon, and allowing the mixture to cool. The crystals which formed were separated, washed with cold water, and dried. The filtrate was concentrated in a vacuum still, and additional crystals were thus obtained. The yield of sodium strontium galacturonate, $Na\ Sr(C_6H_9O_7)_3 6H_2O$, obtained without the use of an organic solvent, was 1,190 g, or 88.6 percent of the galacturonic acid content of the pectic acid used.

The mother liquor from the first crop of crude sodium strontium galacturonate contains the residual pectic enzymes and may be used for the preparation of additional salt without the use of a new supply of the enzyme preparation. In an expermient similar to that just described, the solution which remained after separation of 1,085 g of sodium strontium galacturonate from the hydrolyzate of 1 kg of pectic acid was mixed with a second kilogram of pectic acid and 150 g of sodium bicarbonate. The mixture was allowed to stand, with occasional stirring, at 40° C. After 2 days, 125 g of strontium carbonate was added, and after a total of 10 days, an additional quantity of 125 g. The mixture was placed in a refrigerator for 1 day, and the crystals, which formed, were separated, washed with cold water, and air-dried. They weighed 1,400 g. Thus the total yield of sodium strontium galacturonate obtained from 2 kg of pectic acid without an evaporation step, or the addition of a second quantity of enzyme, was 2,485 g, or 92.5 percent of the galacturonic acid content of the pectic acid used. When additional pectic acid and sodium bicarbonate were added to the mother liquor, hydrolysis of the pectic acid was very slow, and it thus appeared that the enzyme had become more or less inactive. Upon the addition of a second quantity of Pectinol (50 g), the hydrolysis proceeded as before. Strontium carbonate was added as in the previous hydrolysis, and the resulting sodium strontium galacturonate was separated. Although in continuous operation the enzyme loses its activity and the impurities accumulate in the mother liquor, the crystallizing properties of sodium strontium galacturonate are such that the process may be continued for a considerable period before it is necessary to discard the mother liquors.

2. PREPARATION OF SODIUM STRONTIUM GALACTURONATE FRO CITRUS PECTIN

A mixture of 10 g of dry citrus pectin,[3] 1.25 g of sodium bicarbonat and 1 g of Pectinol was added in portions with stirring to 100 ml water contained in a 200-ml Erlenmeyer flask. The mixture w protected from mold growth by the addition of 5 ml of toluene an allowed to stand in a warm place (25° to 40° C). After 1 week, th mixture was neutralized by the addition of strontium carbonate (3 and heated to boiling to insure complete solution of the product. Th hot solution was filtered with the aid of about 1 g of diatomaceou earth. The filtrate was concentrated in a vacuum still, at a tempe ature below 50° C, to a volume of about 30 ml and was then kep overnight in the refrigerator. The crystals of sodium strontiu galacturonate, which formed, were collected on a filter, washed wit cold water, and dried. The product obtained from 10 g of citru pectin weighed 8.7 g, corresponding to approximately 75 percent the galacturonic acid content of the pectin.[4]

3. PREPARATION OF SODIUM STRONTIUM GALACTURONATE FRO ORANGE PEEL

The peels from Florida oranges were coarsely ground, and washe with cold water to remove the water-soluble constituents. Th washed, moist peel contained 71.3 g of galacturonic acid per kilogra as determined by the CO_2 method. One kilogram of the moist pe was heated to boiling with 2 liters of water, and the mixture was the cooled to 40° C. After the addition of 50 g of Pectinol and 20 ml toluene, the mixture was kept at a temperature of 40° C and stirre occasionally. In the course of the first day, the acidity increased t about pH 3.2 and then remained substantially constant for the re mainder of the hydrolysis period. Since this value does not diffe widely from the optimum for the enzyme, no adjustment of acidit was made. After 7 days, the material was transferred to a filter, an the hydrolyzate was separated from the residue.[5]

An analysis of the hydrolyzate gave the following results:[6]

Soluble solids	131 g/kg of moist peel.
Volatile acid	0. 048 equivalent/kg of moist peel.
Free acid	0. 338 equivalent/kg of moist peel.
Copper-reducing substances	115 g/kg of moist peel.
Galacturonic acid (CO_2 method)	64. 3 g/kg of moist peel.
Arabinose	28 g/kg of moist peel.

The hydrolyzate from 1 kg of orange peel, containing 64.3 g of galac turonic acid, was heated to boiling, and treated with 16.4 g of strontiu carbonate. After the strontium carbonate had reacted, the solutio was cooled, and 9.3 g of sodium bicarbonate was added. The solutio was acidified with acetic acid, and filtered with the aid of a decoloriz

[3] The sample of pectin contained 84 percent of galacturonic acid by analysis. After the first day, th acidity of the mixture should be within the pH range 3.5 to 4.5. With most pectins, the proportions give here are satisfactory.

[4] For student instruction, the presence of the galacturonate radical may be readily demonstrated by th following reaction discovered by Ehrlich [10]: A few milligrams of the salt, dissolved in 2 ml of water, treated with 5 ml of a saturated solution of basic lead acetate. A white precipitate forms, which is solub in an excess of the reagent. When the solution is boiled, the precipitate becomes orange, and finally bric red.

[5] The addition of the pectic enzyme to citrus fruit residues causes a softening or degradation of the ce walls, which facilitates the separation of the oil in the peels. Although removal of the oil is not necessar in the preparation of sodium strontium galacturonate, it may nevertheless be advantageous to separa it prior to filtration, or to use as a raw material, citrus fruit residues from which the oil has been removed.

[6] The analytical methods are described in [3].

ing carbon. The filtrate was concentrated in a vacuum still at 40° C to a volume of 110 ml. During the evaporation, crystals of sodium strontium galacturonate formed. The material was allowed to stand overnight in a refrigerator, and the salt was then collected on a filter, washed with a small quantity of cold water, and dried. The product, substantially pure sodium strontium galacturonate, weighed 58.8 g. The amount corresponds to a yield of 66.7 percent, based on the galacturonic acid content of the hydrolyzate.

4. PREPARATION OF SODIUM STRONTIUM GALACTURONATE FROM GRAPEFRUIT PEEL

The peel of thick-skinned, seedless western grapefruit was coarsely ground in a food chopper and thoroughly washed in a bag suspended for 18 hours in running water. The moist, washed peel, containing 12.7 percent of solids, was heated to boiling with 2 parts of water. The mixture was cooled, treated with one-twentieth part of Pectinol and a small quantity of toluene, and allowed to stand at 40° C. After 10 days, the material was filtered on a Büchner funnel, and the residue was washed with water. The combined filtrate and washings were used for analysis and for the preparation of sodium strontium galacturonate.

An analysis of the hydrolyzate gave the following results:

Soluble solids	79 g/kg of moist peel.
Volatile acid	0. 036 equivalent/kg of moist peel.
Free acid	0. 172 equivalent/kg of moist peel.
Copper-reducing substances	62 g/kg of moist peel.
Galacturonic acid (CO_2 method)	44. 9 g/kg of moist peel.
Arabinose	11 g/kg of moist peel.

The hydrolyzate corresponding to 1 kg of moist peel was heated to boiling and neutralized with 11.5 g of strontium carbonate and 6.5 g of sodium bicarbonate. By filtration and concentration of the solution, 50.2 g of crystalline sodium strontium galacturonate was obtained. The amount corresponds to a yield of 81.6 percent, based on the galacturonic acid content of the hydrolyzate.

A similar experiment conducted on the unwashed peel, containing 19.3 percent of total solids, yielded a hydrolyzate that gave the following results:

Soluble solids	148 g/kg of moist peel.
Volatile acid	0. 027 equivalent/kg of moist peel.
Free acid	0. 170 equivalent/kg of moist peel.
Copper-reducing substances	136 g/kg of moist peel.
Galacturonic acid (CO_2 method)	29. 8 g/kg of moist peel.
Arabinose	6 g/kg of moist peel.

The hydrolyzate corresponding to 1 kg of the moist peel was treated with 7.5 g of strontium carbonate and 4.3 g of sodium bicarbonate. By concentration of the solution, 15 g of sodium strontium galacturonate was obtained. This amount corresponds to 36.7 percent of the galacturonic acid content of the hydrolyzate. The mother liquors contained a large amount of reducing substances which require further study.

5. PREPARATION OF GALACTURONIC ACID FROM SODIUM STRONTIUM GALACTURONATE

One mole of sodium strontium galacturonate (798.2 g) was added with stirring to 1,500 ml of aqueous 2 *N* sulfuric acid.[7] The solution was filtered to remove the strontium sulfate, and was then concentrated to a volume of 900 ml in a vacuum still at a temperature of 40° C. The strontium sulfate that separated during the evaporation was removed by filtration, and the residue on the filter was washed with 100 ml of hot water. The clear filtrate was seeded with crystalline galacturonic acid hydrate and was allowed to cool to room temperature with constant stirring. After crystallization at room temperature was substantially complete, the mixture was placed in a refrigerator for 18 hours. The crystals of galacturonic acid hydrate which formed were collected on a filter and washed with ice water. The crop of galacturonic acid monohydrate, obtained without the use of an organic solvent, weighed 407 g and was substantially pure. The mother liquor was concentrated in a vacuum still to a volume of 400 ml and was then diluted with 1 liter of methyl alcohol. The alcohol was added portion-wise over the space of several hours in order to facilitate crystallization of sodium sulfate. Crystallization was induced by seeding with $Na_2SO_4.10H_2O$. The salt was separated by filtration, washed with methyl alcohol, and discarded. The alcohol filtrate and wash liquor were transferred to a vacuum still and the methyl alcohol was recovered. The sirupy residue (200 ml) from the still was seeded with galacturonic acid hydrate, and the crystals which formed in the course of 1 day were separated by filtration. By concentrating the mother liquor, additional material was obtained. The total yield of crystalline galacturonic acid was 607 g, or 95.4 percent of the theoretical. The acid may be recrystallized readily from water or from aqueous acetic acid, as described in a previous publication [11]. The yield of crystalline acid obtained from the sodium strontium salt is considerably higher than that reported by Link and Nedden from barium galacturonate [5(b)].

III. REFERENCES

[1] H. S. Isbell, J. Research NBS **33,** 45 (1944) RP1594.
[2] H. S. Isbell and H. L. Frush, J. Research NBS **32,** 77 (1944) RP1576.
[3] H. S. Isbell and H. L. Frush, J. Research NBS **33,** 389 (1944) RP1616.
[4] F. Ehrlich, Z. angew. Chem. **40,** 1305 (1927).
[5] (a) K. P. Link and A. D. Dickson, J. Biol. Chem. **86,** 491 (1930).
(b) K. P. Link and R. Nedden, J. Biol. Chem. **94,** 307 (1931).
(c) S. Morrell, L. Baur, and K. P. Link, J. Biol. Chem. **105,** 15 (1934).
[6] H. H. Mottern and H. L. Cole, J. Am. Chem. Soc. **61,** 2701 (1939).
[7] E. Rietz and W. D. Maclay, J. Am. Chem. Soc. **65,** 1242 (1943).
[8] H. D. Poore, Ind. Eng. Chem. **26,** 637 (1934).
[9] K. U. Lefèvre and B. Tollens, Ber. deut. chem. Ges. **40,** 4513 (1907).
[10] F. Ehrlich, Ber. deut. chem. Ges. **65,** 352 (1932).
[11] H. S. Isbell and H. L. Frush, J. Research NBS **31,** 33 (1943) RP1547.

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[7] For satisfactory results an excess of sulfuric acid must be avoided; a small excess of the salt is not objectionable.